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(71) Applicant: INTEGUMENT TECHNOLOGIES, INC. [US/US]; 10 East Fourth Street, Jamestown, NY 14701 (US).													
(72) Inventors: KOLOSKI, Timothy, S.; Apartment 3, 4333 Chestnut Ridge Road, West Amherst, NY 14228 (US). VARGO, Terrence, G.; 15 Landers Road, Kenmore, NY 14217 (US).													
(74) Agents: ROGALSKYJ, Peter et al.; Nixon, Hargrave, Devans & Doyle LLP, Clinton Square, P.O. Box 1051, Rochester, NY 14603 (US).													
(54) Title: POLYMER COMPOSITES AND METHODS FOR MAKING AND USING SAME													
(57) Abstract													
<p>Composites which include a polymer having natural free volume therein and an inorganic or organic material disposed in the natural free volume of the polymer are disclosed. In addition, methods for making a composite are described. A polymer having free volume therein is provided. The free volume is evacuated, and inorganic or organic molecules are infused into the evacuated free volume of the polymer. The inorganic or organic molecules can then be polymerized under conditions effective to cause the polymerized inorganic or organic molecules to assemble into macromolecular networks. Alternatively, where the polymer contains a functionality, the inorganic or organic molecules can be treated under conditions effective to cause the inorganic or organic molecules to interact with the polymer's functionality. Use of the disclosed composites as photoradiation shields and filters, electromagnetic radiation shields and filters, antistatic layers, heterogeneous catalysts, conducting electrodes, materials having flame and heat retardant properties, components in the construction of electrolytic cells, fuel cells, and optoelectronic devices, and antifouling coatings is also described. Oxyhalopolymer composites which include an oxyhalopolymer having free volume therein and an inorganic or organic material disposed in the free volume of the oxyhalopolymer are also disclosed. Also described is a surface-oxyhalogenated non-halopolymer composite. The composite includes a surface-oxyhalogenated non-halopolymer having free volume therein and an inorganic or organic material disposed in the free volume of the surface-oxyhalogenated non-halopolymer. Methods for making and using these oxyhalopolymer composites and surface-oxyhalogenated non-halopolymer composites are also described.</p>													

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POLYMER COMPOSITES AND METHODS FOR MAKING AND USING SAME

The present application claims the benefit of U.S. Provisional Patent Application
5 Serial No. 60/039,258, filed February 26, 1997, U.S. Patent Application Serial No.
08/833,290, filed April 4, 1997, U.S. Patent Application Serial No. 08/955,901, filed
October 22, 1997, and U.S. Patent Application Serial No. 08/997,012, filed December 23,
1997. Each of the above-identified applications is incorporated herein by reference.

FIELD OF THE INVENTION

The present invention relates generally to composites and, more particularly, to
polymer composites containing inorganic or organic materials disposed in the polymer's
free volume and to oxyhalopolymer composites and surface-oxyhalogenated non-
15 halopolymer composites, and to methods of making and using same.

BACKGROUND OF THE INVENTION

Hybrid Materials

20 Inorganic-organic hybrid materials have been used with varying degrees of success
for a variety of applications.

In some of these materials, organic polymers are blended with inorganic fillers to
improve certain properties of those polymers or to reduce the cost of the polymeric
compositions by substituting cheaper inorganic materials for more expensive organic
25 materials. Typically, inorganic fillers are either particulate or fibrous and are derived from
inexpensive materials, such as naturally occurring minerals and glass. For example, U.S.
Patent 5,536,583 to Roberts et al. ("Roberts") describes methods for mixing inorganic
ceramic powders into polyethersulfones, polyether ketones, and polyether ether ketones and
methods for including metal nitrides, oxides, and carbides into fluoropolymer resins to
30 produce corrosion inhibiting coatings as well as coatings which have improved abrasion
resistance and/or enhanced bonding characteristics. U.S. Patent No. 5,492,769 to Pryor et
al. ("Pryor") describes methods for embedding metal or ceramic materials into organic
polymeric materials to increase the polymer's abrasion resistance. U.S. Patent No.
5,478,878 to Nagaoka et al. ("Nagaoka") describes a thermoplastic blend of an organic

polymer and inorganic metallic fillers which improves the polymer's resistance to discoloration upon exposure to ambient light sources.

Each of the above inorganic-organic hybrid materials were made either (1) by melting and then mixing the inorganic and organic phases into a homogeneous mixture which was then cured, extracted, or dried or (2) by dissolving the polymer and inorganic material together in a solvent in which both materials were miscible, mixing to produce a homogeneous solution, and then evaporating the solvent to extract the hybrid material. The resulting inorganic-organic hybrid materials are essentially macromolecular blends which have separate inorganic and organic domains which range from nanometers to tens of micrometers in size. All of the above composites are fabricated by using inorganic materials, typically naturally occurring minerals, which are in thermodynamically stable metallic forms, such as metal oxides, metal nitrides, and zero-valent metals.

These inorganic-organic hybrid materials suffer from a number of drawbacks which limit their utility. For example, the size of the domain that the inorganic materials assume within the hybrid depends on the particle size of the inorganic material particulate or fiber used in making the hybrid. In addition, the homogeneity of the inorganic-organic hybrid material largely depends on either the solubility of the inorganic material in the polymeric melt or on the solubility of the inorganic material in the solvent used to solubilize the polymeric material. Furthermore, the properties and molecular structures of these hybrids depend greatly on the methods used to extrude, cast, or dry the solid hybrid material from the melt or solubilized mixtures, which gives rise to significant, undesirable, and frequently uncontrollable batch-to-batch and regional variations.

Inorganic-organic hybrid materials have also been prepared by dispersing powdered or particulate forms of inorganic materials within various polymeric matrices.

For example, U.S. Patent No. 5,500,759 to Coleman ("Coleman") discloses electrochromic materials made by dispersing electrically conductive metal particles into polymeric matrices; U.S. Patent No. 5,468,498 to Morrison et al. ("Morrison") describes aqueous-based mixtures of colloidal vanadium oxide and dispersed sulfonated polymer which are useful for producing antistatic polymeric coatings; U.S. Patent No. 5,334,292 to Rajeshwar et al. ("Rajeshwar") discloses conducting polymer films containing nanodispersed inorganic catalyst particles; and U.S. Patent No. 5,548,125 to Sandbank ("Sandbank") discloses methods for melt- or thermo-forming flexible polymeric gloves containing particulate tungsten which makes the gloves useful for shielding x-radiation.

Although the inorganic-organic hybrid materials are homogeneously mixed, they contain separate inorganic and organic phases on a macromolecular scale. These separate phases frequently give rise to the inorganic material's migration within and/or leaching out of the polymeric matrix. Furthermore, the inorganic phases of these inorganic-organic hybrid materials can be separated from the polymer matrix by simple mechanical processes or by solvent extraction of the polymer. Consequently, upon exposure to certain temperatures or solvents, the inorganic phases of these hybrids can migrate and dissipate out of or accumulate in various regions within the polymeric matrix, reducing its useful life.

Because of the problems associated with migration and leaching of the inorganic phase in inorganic-organic hybrids, hybrid materials containing inorganic phases having greater stability have been developed. These materials rely on physically entrapping large interpenetrating macromolecular networks of inorganic materials in the polymeric chains of the organic material.

For example, U.S. Patent No. 5,412,016 to Sharp ("Sharp") describes polymeric inorganic-organic interpenetrating network compositions made by mixing a hydrolyzable precursor of an inorganic gel of Si, Ti, or Zr with an organic polymer and an organic carboxylic acid to form a homogeneous solution. The solution is then hydrolyzed, and the resulting hybrid materials are used to impart added toughness to conventional organic polymers as well as to increase their thermal stabilities and abrasion resistances. U.S. Patent No. 5,380,584 to Anderson et al. ("Anderson I") describes an electrostatography imaging element which contains an electrically-conductive layer made of a colloidal gel of vanadium pentoxide dispersed in a polymeric binder. U.S. Patent No. 5,190,698 to Coltrain et al. ("Coltrain I") describes methods for making polymer/inorganic oxide composites by combining a polymer derived from a vinyl carboxylic acid with a metal oxide in a solvent solution, casting or coating the resulting solution, and curing the resulting sample to form a composite of the polymer and the metal oxide. These composites are said to be useful for forming clear coatings or films having high optical density, abrasion resistance, or antistatic properties. U.S. Patent No. 5,115,023 to Basil et al. ("Basil") describes siloxane-organic hybrid polymers which are made by hydrolytic condensation polymerization of organoalkyoxysilanes in the presence of organic film-forming polymers. The method is similar to that described in Sharp and, similarly, is used to improve a polymer's mechanical strength and stability while maintaining its flexibility

and film forming properties. U.S. Patent No. 5,010,128 to Coltrain et al. ("Coltrain II") describes methods for blending metal oxides with etheric polyphosphazenes to increase abrasion resistance and antistatic properties of polyphosphazene films. These methods, like those of Coltrain I, employ inorganic metal precursors which contain hydrolyzable leaving
5 groups.

In each of the foregoing, the polymeric inorganic-organic interpenetrating network compositions are obtained by, sequentially, (1) adding hydrolyzable metals (or hydrolyzed metal gels) into either a polymer melt or a solvent containing a dissolved polymer; (2) adding a hydrolyzing agent or adjusting the pH of the solution to effect hydrolysis; (3)
10 mixing; and (4) curing.

The methods described, however, suffer from several limitations. For example, they are limited to incorporating interpenetrating metal oxide networks into polymers which have similar solubilities as the hydrolyzable metal precursors or the hydrolyzed metal. In addition, because the method involves first mixing the inorganic hydrolyzable metal
15 precursors or the hydrolyzed metal with the organic polymer and then curing the mixture, curing of the inorganic phase and organic phase necessarily occurs simultaneously. Since both the inorganic and organic materials are in intimate contact during the curing process, the organic phase of the resulting hybrid has physical characteristics different from that of the same polymer cured in the absence of an inorganic phase. This makes it difficult and,
20 in many cases, impossible to predict the concentration of inorganic material necessary to preserve the desired properties of the starting organic polymer material or to predict the properties of the resulting hybrid. Typically, crystallinity and/or free volume in the hybrid materials are significantly different than the starting organic polymer materials cured in the absence of the inorganic phase. The methods also have limited utility because they provide
25 no control over the spatial distribution of the inorganic and organic phases within the polymeric inorganic-organic interpenetrating network hybrid. For example, it is difficult and, in many cases, impossible to control which phase dominates the surface of the bulk material or the surface of the free volume within the bulk material. This variability can cause quality control problems as well as limit the usefulness of the hybrid materials with
30 respect to bulk versus surface properties.

Alternatively, it has been demonstrated that inorganic and organic molecules can be impregnated into solid matrices using supercritical fluids.

WO 94/18264 to Perman et al. describes the use of supercritical fluids for impregnating a variety of specific additives into polymer substrates by simultaneously contacting the polymer substrate with the impregnation additive and a carrier liquid, such as water, in the presence of a supercritical fluid. The described method requires that a polymeric material be simultaneously exposed to an impregnation additive and a carrier liquid, and, then, all three of these components are exposed to a supercritical fluid in a high pressure vessel for a sufficient time to swell the polymeric material so that the carrier liquid and impregnation additive can penetrate the swollen polymeric material.

In Clarke et al., J. Am. Chem. Soc., 116:8621 (1994), supercritical fluid is used to impregnate polyethylene with $\text{CpMn}(\text{CO})_3$ using supercritical CO_2 which acts to both solvate the $\text{CpMn}(\text{CO})_3$ and to swell the polyethylene, thus permitting the flow of $\text{CpMn}(\text{CO})_3$ into the free space created in the swollen polymer and into the free volume of the polymeric material.

Watkins et al., Macromolecules, 28:4067 (1995) discloses methods for polymerizing styrene in supercritical CO_2 -swollen poly(chlorotrifluoroethylene) ("PCTFE").

Methods for impregnating polymeric materials with additives using supercritical fluids suffer from a number of important drawbacks. First, the method requires the use of a high pressure apparatus. Second, the method requires that the supercritical fluid or another suitable carrier solvent be available to solvate the additive to be impregnated in the polymer matrix. Third, the method requires that the polymeric material be grossly swollen to permit the additive to penetrate and, thus, to impregnate the polymeric material. This swelling results in large changes in the host polymer's surface and bulk morphology and also results in a lack of control of the final hybrid material's composition. Finally, this method allows no control over the resulting surface properties of the hybrid materials. Together, these changes and lack of control lead to a variety of physical and chemical changes in the host polymer, including changes in properties such as flexibility, crystallinity, and thermal characteristics. Finally, in most cases where supercritical methods are used to impregnate additives into polymeric materials, the impregnated additive can be readily diffused out of the polymeric material by exposure of the polymeric material to supercritical fluid conditions or, in some cases, to various solvents.

For these and other reasons, there remains a need for inorganic-organic polymer composites and for methods of preparing these inorganic-organic polymer composites which do not suffer from the above-described limitations as well as for methods of

preparing these composites which permits control over the surface properties (e.g., watability, reactivity, adhesiveness, and physical and chemical toughness). The present invention is directed to meeting this need.

5 Anti-Fouling Coatings

Man-made structures, such as boat hulls, buoys, drilling platforms, oil production rigs, bridges, piers, locks, and pipes which are immersed in or in intermittent contact with water are prone to fouling by aquatic and marine organisms, such as green and brown algae, barnacles, mussels, and the like. Such structures are commonly made of metal, but
10 may also include other materials, such as concrete, wood, and plastic. On boat hulls, fouling increases the frictional resistance towards movement through the water, with the consequence of reduced speeds and increased fuel costs. On static structures, such as the legs of drilling platforms, oil production rigs, bridges, and piers, the resistance of thick layers of fouling to waves and currents can cause unpredictable and potentially dangerous
15 stresses in the structure. Moreover, fouling also makes it difficult to inspect the structure for defects, such as stress cracking and corrosion. In pipes, such as cooling water intakes and outlets, fouling reduces the pipe's effective cross-sectional area, which results in reduced flow rates.

The commercially most successful method of inhibiting fouling have involved the
20 use of anti-fouling coatings which release substances toxic to aquatic or marine life, for example tributyltin chloride or cuprous oxide. Such coatings, however, are being regarded with increasing disfavor because of the damaging effects these toxins can have on the aquatic or marine environment into which they are released. There is, accordingly, a need for anti-fouling coatings which do not release toxic materials.

25

SUMMARY OF THE INVENTION

The present invention relates to a composite. The composite includes a polymer having a natural free volume therein and an inorganic or organic material disposed in the
30 polymer's natural free volume.

The present invention also relates to a method for making a composite. A polymer having free volume therein is provided. The free volume of the polymer is evacuated, and inorganic or organic molecules are infused into the polymer's evacuated free

volume. In a particularly preferred embodiment of the present invention, the inorganic or organic molecules are then polymerized under conditions effective to assemble the inorganic or organic molecules into macromolecular networks. In an alternative particularly preferred embodiment of the present invention, the polymer comprises a functionality, and the inorganic or organic molecules are treated under conditions effective to cause the inorganic or organic molecules to interact with the polymer's functionality.

The present invention also relates to a method for preventing fouling of a surface by organisms. The method includes applying, to the surface, a composite that includes a polymer having free volume therein and an inorganic or organic material disposed in the polymer's free volume.

The present invention also relates to a method for preventing fouling of a polymer surface by organisms. The polymer surface includes a polymer having free volume therein. The polymer's free volume is evacuated, and inorganic or organic molecules are infused into the evacuated free volume.

The present invention also relates to an object. The object has a surface, all or a portion of which comprises a polymer. The polymer has free volume therein, and an inorganic or organic material is disposed in the polymer's free volume.

The present invention also relates to a method for making an oxyhalopolymer composite. The method includes providing an oxyhalopolymer which has free volume therein. The oxyhalopolymer's free volume is evacuated, and inorganic or organic molecules are infused into the evacuated free volume of the oxyhalopolymer.

The present invention also relates to another method for making an oxyhalopolymer composite. In this method, a halopolymer composite is provided. The halopolymer composite's surface halogen atoms are then modified under conditions effective to substitute at least a portion of the halopolymer composite's surface halogen atoms with hydrogen atoms and oxygen atoms or oxygen-containing radicals.

The present invention also relates to a method for making a surface-oxyhalogenated non-halopolymer composite. The method includes providing a surface-oxyhalogenated non-halopolymer having free volume therein. The method further includes evacuating the free volume of the surface-oxyhalogenated non-halopolymer, and infusing inorganic or organic molecules into the evacuated free volume of the surface-oxyhalogenated non-halopolymer.

The present invention also relates to another method for making a surface-oxyhalogenated non-halopolymer composite. In this method, a surface-halogenated non-halopolymer composite is provided. The method further includes modifying the surface-halogenated non-halopolymer composite's surface halogen atoms under conditions effective
5 to substitute at least a portion of the surface-halogenated non-halopolymer composite's surface halogen atoms with hydrogen atoms and oxygen atoms or oxygen-containing radicals.

The present invention, in another aspect thereof, is related to an oxyhalopolymer composite. The oxyhalopolymer composite includes an oxyhalopolymer having free
10 volume therein and an inorganic or organic material disposed in the free volume of the oxyhalopolymer.

The present invention also relates to a surface-oxyhalogenated non-halopolymer composite. The composite includes a surface-oxyhalogenated non-halopolymer having free volume therein and an inorganic or organic material disposed in the free volume of the
15 surface-oxyhalogenated non-halopolymer.

The composites of the present invention contain polymeric phases which have physical properties substantially similar to the properties of the native polymer (i.e., polymer in the absence of inorganic or organic molecules or macromolecular networks). Consequently, the composites of the present invention, relative to conventional inorganic-
20 organic hybrid materials, have significantly more predictable mechanical properties. The composites of the present invention also have controllable, predictable, and reproducible levels of optical densities and electrical, ionic, and charged species conductivities, which make them useful in various applications including photoradiation shields and filters, electromagnetic radiation shields and filters, heterogeneous catalytic substrates, and
25 conducting electrodes. These characteristics also make these composites useful as components in the construction of electrolytic cells, fuel cells, optoelectronic devices, semiconductors for microelectronic applications, and materials having flame and heat retardant properties.

Although the initial formation of these composites results in materials having
30 physical properties substantially similar to those of the native polymer, subsequent thermal, chemical, photochemical, or electrochemical treatment of the composites produced in accordance with the present invention can lead to improved physical properties. It is believed that these changes in the physical properties of the composite result from chemical

and/or electronic interactions between the infused inorganic or organic molecules and the polymer.

In addition, composites of the present invention can have a surface which optionally contains halogen atoms, a portion of which have been replaced with hydrogen atoms and oxygen atoms or oxygen-containing groups. The oxyhalopolymer surface retains many of the positive attributes characteristic of halopolymer surfaces, such as tendency to repel water and other polar solvents, high thermal stability, and low adhesion and friction coefficients. However, unlike halopolymer surfaces, the surfaces of the oxyhalopolymer composites of the present invention have reactive chemical sites which permit bonding with other chemical functionalities, such as organosilicons, organometallic precursors, transition metal ions and compounds, transition metal films, fluorescent compounds and other dyes, and biological materials, such as proteins, enzymes, and nucleic acids. In addition, by proper choice of the infused inorganic material and chemical functionality at the surface, polymer composites having an inorganic surface which is the same as, similar to, or different from the infused inorganic material can be prepared. Such materials are useful, for example, in preparing metal oxide/fluoropolymer composites having a pure metal oxide surface.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagram illustrating the results of infusion of halopolymer composites.

Figure 2 is a diagram illustrating a cross-sectional view of an oxyhalopolymer composite of the present invention.

Figure 3 is a preparative scheme for making an oxyhalopolymer composite in accordance with the present invention.

Figure 4 is another preparative scheme for making an oxyhalopolymer composite in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a composite. The composite includes a polymer which has natural free volume therein and an inorganic or organic material disposed in the natural free volume of the polymer.

The polymer can be an organic based polymer or an inorganic-organic hybrid polymer. Organic based polymers suitable for use in the composites of the present invention can be homopolymers, copolymers, multicomponent polymers, or combinations thereof. Suitable organic polymers include halopolymers, such as fluoropolymers and fluorochloropolymers, polyimides, polyamides, polyalkylenes, such as polyethylene, polypropylene, and polybutylene, poly(phenylenediamine terephthalamide) filaments, modified cellulose derivatives, starch, polyesters, polymethacrylates, polyacrylates, polyvinyl alcohol, copolymers of vinyl alcohol with ethylenically unsaturated monomers, polyvinyl acetate, poly(alkylene oxides), vinyl chloride homopolymers and copolymers, terpolymers of ethylene with carbon monoxide and with an acrylic acid ester or vinyl monomer, polysiloxanes, polyfluoroalkylenes, poly(fluoroalkyl vinyl ethers), homopolymers and copolymers of halodioxoles and substituted dioxoles, polyvinylpyrrolidone, or combinations thereof. Halopolymers are organic polymers which contain halogenated groups, such as fluoroalkyl, difluoroalkyl, trifluoroalkyl, fluoroaryl, difluoroalkyl, trifluoroalkyl, perfluoroalkyl, perfluoroaryl chloroalkyl, dichloroalkyl, trichloroalkyl, chloroaryl, dichloroalkyl, trichloroalkyl, perchloroalkyl, perchloroaryl, chlorofluoroalkyl, chlorofluoroaryl, chlorodifluoroalkyl, and dichlorofluoroalkyl groups. Halopolymers include fluorohydrocarbon polymers, such as polyvinylidene fluoride ("PVDF"), polyvinylfluoride ("PVF"), polychlorotetrafluoroethylene ("PCTFE"), polytetrafluoroethylene ("PTFE") (including expanded PTFE ("ePTFE")). Fluoropolymers are preferred for many applications because of their extreme inertness, high thermal stability, hydrophobicity, low coefficients of friction, and low dielectric properties. In addition to retaining these desirable properties, in many applications, particularly catalytic applications, it is advantageous to utilize the highly electronegative characteristics of these fluoropolymers for enhancing the catalytic properties of metals by associating these metals with the fluoropolymers. Suitable fluoropolymers include perfluorinated resins, such as perfluorinated siloxanes, perfluorinated styrenes, perfluorinated urethanes, and copolymers containing tetrafluoroethylene and other perfluorinated oxygen-containing polymers like

perfluoro-2,2-dimethyl-1,3-dioxide (which is sold under the trade name TEFLON-AF). Other polymers which can be used in the composites of the present invention include perfluoroalkoxy-substituted fluoropolymers, such as MFA (available from Ausimont USA (Thoroughfare, New Jersey)) or PFA (available from Dupont (Willmington, Delaware)),
5 polytetrafluoroethylene-co-hexafluoropropylene ("FEP"), ethylenechlorotrifluoroethylene copolymer ("ECTFE"), and polyester based polymers, examples of which include polyethyleneterphthalates, polycarbonates, and analogs and copolymers thereof.

Polyphenylene ethers can also be employed. These include poly (2,6-dimethyl-1,4-phenylene ether), poly(2,6-diethyl-1,4-phenylene ether), poly(2-methyl-6-ethyl-1,4-phenylene ether), poly(2-methyl-6-propyl-1,4-phenylene ether), poly(2,6-dipropyl-1,4-phenylene ether), poly(2-ethyl-6-propyl-1,4-phenylene ether), poly(2,6-dibutyl-1,4-phenylene ether), and the like.
10

Examples of suitable polyamides include polyhexamethylene alipamide (nylon 66), polyhexamethylene azelamide (nylon 69), polyhexamethylene sebacamide (nylon 610),
15 polyhexamethylene dodecanoamide (nylon 612), poly-bis-(p-aminocyclohexyl) methane dodecanoamide, polytetramethylene alipamide (nylon 46) and polyamides produced by ring cleavage of a lactam such as polycaprolactam (nylon 6) and polylauryl lactam. Furthermore, there may be used polyamides produced by polymerization of at least two amines or acids used for the production of the above-mentioned polymers, for example,
20 polymers produced from adipic acid, sebacic acid and hexamethylenediamine. The polyamides further include blends of polyamides such as a blend of nylon 66 and nylon 6 including copolymers such as nylon 66/6.

Aromatic polyamides may also be used in the present invention. Preferably they are incorporated in copolyamides which contain an aromatic component, such as melt-
25 polymerizable polyamides containing, as a main component, an aromatic amino acid and/or an aromatic dicarboxylic acid such as para-aminoethylbenzoic acid, terephthalic acid, and isophthalic acid.

Typical examples of the thermoplastic aromatic copolyamides include copolymer polyamide of p-aminomethylbenzoic acid and ϵ -caprolactam (nylon AMBA/6), polyamides
30 mainly composed of 2,2,4-/2,4,4-trimethylhexamethylene-diamineterephthalamide (nylon TMDT and Nylon TMDT/6I), polyamide mainly composed of hexamethylene diamineisophthalamide, and/or hexamethylenediamineterephthalamide and containing, as another component, bis(p-aminocyclohexyl)methaneisophthalamide and/or bis(p-

aminocyclohexyl) methaneterephthalamide, bis(p-aminocyclohexyl)propaneisophthalamide and/or bis(p-aminocyclohexyl)propaneterephthalamide, (nylon 6I/PACM I, nylon 6I/DMPACM I, nylon 6I/PACP I, nylon 6I/6T/PACM I/PACM T, nylon 6I/6T/DMPACM I/DMPACM T, and/or nylon 6I/6T/PACP I/PACP T).

5 Styrene polymers can also be used. These include polystyrene, rubber modified polystyrene, styrene/acrylonitrile copolymer, styrene/methylmethacrylate copolymer. ABS resin, styrene/alphamethyl styrene copolymer, and the like.

Other suitable representative polymers include, for example, poly(hexamethylene alipamide), poly(ϵ -caprolactam), poly(hexamethylene phthalamide or isophthalamide),
10 poly(ethylene terephthalate), poly(butylene terephthalate), ethylcellulose and methylcellulose, poly(vinyl alcohol), ethylene/vinyl alcohol copolymers, tetrafluoroethylene/vinyl alcohol copolymers, poly(vinyl acetate), partially hydrolyzed poly(vinyl acetate), poly(methyl methacrylate), poly(ethyl methacrylate), poly(ethyl acrylate), poly(methyl acrylate), ethylene/carbon monoxide/vinyl acetate terpolymers,
15 ethylene/carbon monoxide/methyl methacrylate terpolymers, ethylene/carbon monoxide/n-butyl acrylate terpolymers, poly(dimethylsiloxane), poly(phenylmethylsiloxane), polyphosphazenes and their analogs, poly(heptafluoropropyl vinyl ether), homopolymers and copolymers of perfluoro(1,3-dioxole) and of perfluoro(2,2-dimethyl-1,3-dioxole), especially with tetrafluoroethylene and optionally with another ethylenically unsaturated
20 comonomer, poly(ethylene oxide), poly(propylene oxide), and poly(tetramethylene oxide).

These and other suitable polymers can be purchased commercially. For example, poly(phenylenediamine terephthalamide) filaments can be purchased from Dupont under the tradename KEVLAR™. Alternatively, polymers suitable for the practice of the present invention can be prepared by well known methods, such as those described in Elias,
25 Macromolecules - Structure and Properties I and II, New York:Plenum Press (1977) ("Elias"), which is hereby incorporated by reference.

The polymer can, alternatively, be an inorganic-organic hybrid polymer or blend of organic polymer and inorganic-organic hybrid polymer. Inorganic-organic hybrid polymers suitable for the practice of the present invention include those prepared by
30 conventional methods for making organic-inorganic hybrid materials, such as those described in Roberts, Pryor, Nagaoka, Coleman, Morrison, Rajeshwar, Sandbank, Sharp, Anderson I, Basil, and Coltrain I and II, which are hereby incorporated by reference.

The polymer, in addition to an organic based polymer or an inorganic-organic hybrid polymer, can contain a variety of materials which are known in the art to modify the properties of the polymer. These include, fillers, cross-linking agents, stabilizers, radical scavengers, compatibilizers, antistatic agents, dyes, and pigments. Their inclusion or exclusion will depend, of course, on the use to which the composite will be put, as will be apparent to one skilled in the art.

The materials which make up the polymer, be they an organic polymer or an inorganic-organic hybrid material, contain natural free volume.

The polymer can be of any form suitable for the use to which the composite is to be put. For example, the polymer can be an organic based polymer resin, powder, or particulate or, alternatively, an inorganic-organic hybrid polymer resin, powder, or particulate. Suitable particulate forms include sheets, fibers, or beads. As used herein, sheets are meant to include films, fibers are meant to include filaments, and beads are meant to include pellets. Beads having diameters of from about 0.1 mm to about several mm (e.g., from about 0.1 mm to about 0.5 mm) and powders having diameters of from about 10 nm to about 0.1 mm and made from PVDF, PTFE, FEP, ECTFE, PFA, or MFA are particularly useful in many applications.

Alternatively, the polymer can be of a form that is different from the one desired for the composite. The inorganic or organic materials are infused into resins in the form of polymer powders, beads, or the like. The infused polymer powders, beads, etc. can then be processed by conventional polymer processing methods into the desired shape. For example, the infused polymer powders, beads, etc. can be extruded into finished sheets or fibers. Alternatively, the infused polymer powders, beads, etc. can be applied to solid objects, such as walls and boat hulls by, for example, spraying, sputtering, or painting (e.g., brushing or rolling) the infused polymer powders, beads, or pellets onto the object under conditions effective to produce a thin film or coating of the infused polymer on the object.

The composites of the present invention, particularly those in the form of beads, sheets, or fibers, can be infused uniformly or non-uniformly. For example, the present invention includes a sheet having two opposing surfaces where the portion of the sheet in proximity to one surface is infused while another portion of the sheet in proximity to the opposite surface is not. This non-uniform infusing can be carried out, for example, by covering one of the sheet's surfaces with a material that prevents evacuation of the free

volume in proximity to the covered surface or, alternatively or additionally, that prevents the infusing material from contacting the covered surface.

For purposes of this invention, free volume is used in a manner consistent with the description of free volume in Elias at pp. 186-188, which is hereby incorporated by
5 reference. Briefly, Elias points out that, by definition, no extensive long-range order can exist in amorphous regions. Elias further notes that these amorphous regions are not x-ray crystalline, and, although studies suggest that x-ray amorphous polymers may have certain order, a definite number of vacant sites must be present. Thus, free volume, as used herein, relates to the vacant sites which are present in amorphous regions of a polymer and into
10 which organic or inorganic molecules can diffuse. The free volume is exploited in accordance with the present invention as regions into which inorganic or organic materials can be introduced, such as by diffusion, and subsequently assembled into macromolecular networks or stabilized through interaction with the polymer's functionality. These free volumes generally form during the curing process, such as upon evaporation of the solvent
15 in which the polymer was formed, but the present invention is not intended to be limited by the mechanism by which the free volume comes to exist in the polymer.

For purposes of this invention, free volumes can be natural free volumes or created free volumes. Natural free volumes, as used herein, relates to the vacant sites which are characteristically present in amorphous regions of a polymer and into which
20 organic or inorganic molecules can diffuse. These natural free volumes include those which are formed during the curing process, such as upon evaporation of the solvent in which the polymer was formed. In contrast, created free volumes are those free volumes which are produced or modified subsequent to the formation of the polymer by exposing the polymer to supercritical fluids under supercritical conditions. Since the free volumes of
25 the composites of the present invention are natural free volumes and do not contain created free volumes, these natural free volumes contain substantially no carrier liquid or other solvent used in supercritical infusion processes.

The total natural free volume available for diffusing inorganic or organic molecules in a particular polymer is dependent on a variety of characteristics of the natural
30 free volume. These include the size, size distribution, concentration, and spatial distribution of the natural free volume, all of which are effected by the conditions under which the polymer was formed, including, for example: how the solvent was removed; the pressure and temperature (and variations therein) during the solvent removal process; the

degree to which the polymer was cured prior to onset of the solvent removal process; the nature of the solvent; the nature of the organic or inorganic-organic hybrid polymer; the size of the polymer matrix; and the like. Another factor affecting the natural free volume of the polymer is the degree of crystallinity. Polycrystalline regions contained within a polymer have less natural free volume than amorphous regions, are tightly packed, and inhibit movement of inorganic molecules into the polymer. Thus, it is preferred that the polymer have at least some degree of non-crystallinity (i.e., that it have a crystallinity of less than 100%). Suitable polymers (e.g., halopolymers and non-halopolymers) are those which have crystallinities of less than 99%, preferably less than 95%. The total natural free volume of the polymer (i.e., the collective volume of the natural free volumes) (" V_s ") is preferably greater than about 1×10^{-6} of the total volume of the polymer. Expressed differently, if the total volume of the polymer is designated V_c , then the collective volume of the natural free volume is preferably greater than about $1 \times 10^{-6} V_c$, more preferably from about $1 \times 10^{-6} V_c$ to about $0.1 V_c$, and still more preferably from about $1 \times 10^{-3} V_c$ to about $0.1 V_c$.

The natural free volume can be an inherent property of the polymer (i.e., a property which is established by the method used to initially form the polymer) or, alternatively, it can be controlled after formation of the polymer by any suitable means (other than by exposure to supercritical fluids under supercritical conditions), such as by increasing or decreasing the temperature of the polymer when the inorganic or organic materials are diffused thereinto. For example, increasing the temperature at which the inorganic or organic molecules are diffused into the polymer increases the natural free volume of the polymer without substantially altering its physical and mechanical properties. Thus, a greater concentration of the inorganic or organic molecules can be diffused into the polymer, which results in, for example, a greater concentration of the macromolecular network in the polymer.

Methods for determining the natural free volume as a fraction of the total polymer volume (i.e., V_s/V_c) are well known to those skilled in the art. Illustrative methods can be found in Elias at pp. 256-259, which is hereby incorporated by reference. The polymer's natural free volume can also be determined by the flow rate of gases through the polymer. Natural free volume and its distribution in the polymer can also be determined by using a photoreactive probe, such as the one described in Horie, "Dynamics of Electron-Lattice Interactions," in Tsuchida, ed., Macromolecular Complexes: Dynamic Interactions and

Electronic Processes, New York:VCH Publishers, pp. 39-59 (1991), which is hereby incorporated by reference.

As indicated above, the composite of the present invention further includes an inorganic or organic material which is disposed in the polymer's natural free volume. The amount of the inorganic or organic material within the natural free volume is typically proportionate to the internal surface area of the starting polymer's natural free volume, which, as described above, can be an inherent characteristic of the polymer or can be controlled by any suitable means (other than by exposure to supercritical conditions), for example, by increasing or decreasing the temperature at which the inorganic or organic material is diffused thereinto. The inorganic material can fill the polymer's natural free volume or occupy a significant portion thereof in two or three dimensions. The inorganic material can itself form three dimensional networks within the polymer's natural free volume. These three dimensional networks can be dense, substantially filling all the natural free volume, or they can be porous, thus permitting the flow of gas molecules into and out of the natural free volume and through the three dimensional inorganic or organic macromolecular network. Alternatively, the inorganic material can be a two-dimensional layer (such as a coating or film) on or along the surface or a portion of the surface of the natural free volume. In the case where the natural free volume is small, the inorganic or organic material may follow the one-dimensional template of the starting material. This results in a two-dimensional morphology depending on the inherent chemistry and/or the physical morphology at the natural free-volume/polymer interfaces. Preferably, the inorganic or organic material is homogeneously or substantially homogeneously spread throughout the entire natural free volume of the polymer.

Any suitable inorganic material can be employed. Preferred inorganic materials suitable for use in the practice of the present invention are those capable of having a vapor pressure greater than zero at a temperature between room temperature and the thermal decomposition temperature of the polymeric material and/or at pressures of from about 0.1 mTorr to about 10 Torr. By inorganic material, it is meant that the material contains at least one metal ion or atom. As used herein, all atoms, other than hydrogen, oxygen, fluorine, chlorine, bromine, helium, neon, argon, krypton, xenon, and radon are considered to be metal atoms. Preferred metal atoms are the alkali metals, the alkaline earth metals, the transition elements, the lanthanides, the actinides, boron, aluminum, gallium, indium, thallium, silicon, germanium, tin, lead, phosphorous, arsenic, antimony, bismuth, selenium.

tellurium, polonium, and astatine. In addition, carbon, nitrogen, sulfur, and iodine are considered metals, particularly in cases where they are bonded to other atoms via non-covalent bonds (e.g., ionic bonds and pi-pi bonds). Particularly useful inorganic materials are those which contain a metal selected from the group consisting of V, W, Fe, Ti, Si, Al, P, Sb, As, Ba, B, Cd, Ca, Ce, Cs, Cr, Co, Cu, Ga, Ge, In, Pb, Mg, Hg, Mo, Ni, Nb, Re, Ta, Tl, Sn, Ir, Rh, Th, Ru, Os, Pd, Pt, Zn, Au, Ag, and combinations thereof. Illustrative inorganic materials contemplated for use in the present invention also include metal ions or metal atoms which contain at least one active ligand. These metal ions or metal atoms which contain at least one active ligand can be polymerized to form a bond to a neighboring metal atom or ion, thereby forming a macromolecular complex, or they can be treated so that they interact with a functionality contained in the polymer to form, for example, a metal species stabilized via complexation by the polymer's functionality. Such metal ions or metal atoms include metallo-oxo species, metallo-nitro species, pi-allyl and arene complexes of Group IIIa, IVa, Va, VIa, VIIa, and VIIIa metals, and organo-metallo complexes ligated to organic functionalities like chlorides, bromides, alkyls, aryls, carboxylic acids, carbonyls, alkoxides, pyridines, tetrahydrofurans, and the like.

Preferably, the inorganic material is in the form of a macromolecular network or interacted with a functionality contained within the polymer. The macromolecular networks and interacted inorganic materials are preferably stable to diffusion out of the polymer at temperatures at which the composite is to be employed. For example, where the composite of the present invention is to be used as a catalyst, it is advantageous that the inorganic macromolecular network or inorganic material interacted with a functionality contained within the polymer be stable to diffusion at temperatures employed in carrying out the particular catalytic reaction.

Suitable functionalities with which the inorganic material can interact include halogens (such as fluorines or chlorines), amines, alkenes, alkynes, carbonyls (such as keto groups, aldehyde groups, carboxylic acid groups, ester groups, amide groups, and the like), alcohols, and thiols. Inorganic molecules which are interacted with functionalities on the polymer can have the formula M^y-X_j , where X is a functionality contained within the polymer (e.g., halogen, such as F or Cl, NH_2 , NH, O-C=O, C-OH, C=C, C≡C, or C=O), y is the oxidation state of the metal, which can range from zero to the highest oxidation state of the particular metal, and j is the number of ligands to which the particular metal can ligate within a given polymer. For example, where M is Pd, and X is Cl, j can be 2.

Illustrative inorganic macromolecular networks which are stable to diffusion include metal atoms and macromolecular networks. Macromolecular networks, as used herein, are molecules containing three or more, preferably more than about 20, more preferably more than about 100, metal atoms that are directly or indirectly bonded together.

5 Suitable macromolecular networks include polycondensates, such as those having the formula $[X(O)_n-O_y-X(O)_n]_m$, wherein m is an integer from about 1 to about 10,000 or more; X represents a metal ion having a charge of $+s$; s is an integer from 1 to the metal's highest attainable oxidation state; y is an integer from 0 to s ; and n is between zero and $s/2$. The well-known silica, titania, and zirconia structures, in which each metal atom is
10 bonded to four oxygen atoms and each oxygen atom is bonded to two metal atoms, are examples of such macromolecular networks. Other macromolecular networks, such as those in which one or two of the bonds to some of the metal atoms in a silica, titania, or zirconia network are occupied by other moieties, such as alkyl groups, are also contemplated. Other macromolecular networks include those formed from pi-allyl
15 compounds, such as pi-allyl compounds of Group IIIa, IVa, Va, VIa, VIIa, and VIIIa metals. Illustrative pi-allyl compounds suitable for use in the practice of the present invention are described, for example, in Wilke et al., Angewandte Chemie, International Edition, 5(2):151-266 (1996), which is hereby incorporated by reference. In particular, these compounds are contemplated as being useful for forming conductive zero-valent
20 macromolecular metal networks (e.g. macro molecular networks of conducting metals in the zero oxidation states), such as those having the formula $(M^0-M^0)_n$, wherein n is from about $\frac{1}{2}$ to about 10,000 and M^0 is a Group IIIa, IVa, Va, VIa, VIIa, or VIIIa metal.

Any suitable organic material can also be employed. Preferred organic materials suitable for use in the practice of the present invention are those capable of having a vapor
25 pressure greater than zero at a temperature between room temperature and the thermal decomposition temperature of the polymeric material. It is preferred that they also be capable of polymerizing into a macromolecular network (e.g., macromolecular networks having the formula $(R-R)_n$, wherein n is an integer from about 1 to about 10,000 and R is a monomer radical), such as through an oxidation, hydrolysis, chemical, electrochemical, or
30 photochemical process. Organic molecules, such as pyrrole, aniline, and thiophene, that can be oxidatively polymerized, such as to form polypyrrole, polyaniline, and polythiophene, are suitable. Other suitable organic molecules are those which can be polymerized by exposure to actinic radiation (e.g., ultraviolet radiation), such as acetylene,

which when polymerized forms polyacetylene. Still other illustrative organic molecules include organic monomers which can be converted to organic macromolecules, (i.e., polymers). These include the entire class of organic monomers which can be polymerized to form polymers, such as conducting polymers. A list of these materials, their properties, and their application to the construction of polymeric batteries, electric capacitors, electrochromic devices, transistors, solar cells, and non-linear optical devices and sensors can be found in Yamamoto, "Macromolecular Complexes: Dynamic Interactions and Electronic Processes", in E. Tsuchida, ed., Sequential Potential Fields in Electrically Conducting Polymers, New York:VCH Publishers, pp. 379-396 (1991) ("Yamamoto"), which is hereby incorporated by reference.

Because of the close proximity of the polymer and the inorganic or organic macromolecular network which exists within the natural free volume therein, the chemical functionality contained at the surface of the free volume within the polymer can, in some instances, influence the chemical and electronic characteristics of the inorganic or organic macromolecular network and *vice versa*. Thus, by altering the polymer, the properties of the inorganic or organic macromolecular network can be influenced. The degree of this influence depends on the nature of the chemistry and electronic properties of the starting polymer. For example, strongly electron-withdrawing atoms, such as fluorine atoms, influence the catalytic properties of many metals. More particularly, Kowalak et al., Collect. Czech. Chem. Commun., 57:781-787 (1992), which is hereby incorporated by reference, reports that fluorinating zeolites containing polyvalent metal cations increases these zeolites' activity for inducing acid catalyzed reactions. Therefore, where the composites of the present invention are to be used for their catalytic properties, it can be advantageous to employ polymeric materials bearing strongly electron-withdrawing groups. In some cases, the polymer can contain pendant groups or chemical functionalities located at the free volume interface which can influence the chemical or electronic properties of the inorganic or organic macromolecular network formed in the free volume. The interactions of the pendant groups or chemical functionalities with the macromolecular network contained in the natural free volume can be via through-space interactions (i.e., no actual bond or complex formation between the interacting species), via direct ionic, hydrogen, or covalent bonding, or, in some cases, via the formation of a bond which is commonly found when metal atoms coordinate with non-metals or other metallic atoms or groups. The formation of such bonds between the polymer material and the macromolecular network

contained within the polymer material's natural free volume can be detected using methods well known to those skilled in the art, such as ultraviolet-visible spectroscopy, infrared spectroscopy, X-ray photoelectron spectroscopy, nuclear magnetic resonance spectroscopy, and other techniques, including those described in Drago, Physical Methods in Chemistry,

5 Philadelphia:W. B. Saunders (1977), which is hereby incorporated as reference.

One of the advantages of composites of the present invention is that many of the properties of the starting polymer are substantially preserved. In contrast to the results obtained by supercritical impregnation methods (which have the effect of swelling the polymer material), preferred composites of the present invention (e.g., composites which
10 contain inorganic or organic macromolecular networks disposed in the natural free volume of a polymer) have dimensions which are substantially equal to the dimensions of the starting polymer (i.e., the polymer whose natural free volume contains no inorganic or organic macromolecular networks disposed therein). Preferred composites of the present invention also have flexibility, crystallinity, or thermal decomposition temperatures ("Td")
15 which are substantially the same as the flexibility, crystallinity, or Td of the starting polymer. As used in this context, properties which differ by less than 10 % are contemplated as being substantially the same. Td is described in Elias, Macromolecules - Structure and Properties, I and II, New York:Plenum Press (1977), which is hereby incorporated by reference. In other situations, it may be desirable to modify these
20 properties so that they are different than those of the starting polymer material. This can be done by choosing an appropriate inorganic or organic molecule. Alternatively or additionally, this can be achieved by subsequent chemical, photochemical, electrochemical, or thermal treatments which can act to initiate interactions between the chemical functionalities of the infused organic or inorganic macromolecular network and the
25 chemical functionalities found at the free volume surface of the polymer. These interactions can lead to, for example, enhanced catalytic activity of metal species in the macromolecular network, enhanced thermal properties of the composite compared with the initial thermal properties of the starting polymer, or enhanced conductivity of an organic conducting macromolecular network. To enhance the conductivity of organic conducting
30 macromolecular networks, the macromolecular network can be doped, for instance, by the chemistry contained in the polymeric material (especially the chemical functionalities of the polymer at the free volume interface) or, alternatively, by a subsequent diffusion of dopant, whereby a dopant molecule is incorporated into the composite. Suitable dopants that can

be used to enhance the conductivity of conducting macromolecular networks disposed in the composites of the present invention can be found, for example, in Yamamoto, which is hereby incorporated by reference.

Although, as indicated above, preferred inorganic materials are those which are
5 resistant to diffusion, the present invention is not intended to be limited thereto. For example, the inorganic material can be a compound which can be converted, such as by chemical (e.g. oxidation, hydrolysis or hydrogenation), or electrochemical, photochemical, or thermal methods, to an inorganic macromolecular network or to a metal species interacted with the polymer's functionality which resists diffusion. For example, the
10 inorganic material can be a compound selected from the groups consisting of VOCl_3 , $\text{W}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$, TiCl_4 , SiCl_4 , AlCl_3 , PCl_3 , SbCl_5 , $\text{As}(\text{C}_2\text{H}_5)_3$, $\text{Ba}(\text{C}_3\text{H}_7)_2$, borane pyridine and tetrahydrofuran complexes, $\text{Cd}(\text{BF}_4)_2$, $\text{Ca}(\text{OOCCH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9)_2$, cerium (III), 2-ethylhexanoate, cesium 2-ethylhexoxide, chromium (III) naphthenate, CrO_2Cl_2 , $\text{Co}(\text{CO})_3\text{NO}$, copper (II) dimethylaminoethoxide, triethylgallium, GeCl_4 , triethylindium, lead naphthenate,
15 $\text{C}_2\text{H}_5\text{MgCl}$, $(\text{CH}_3)_2\text{Hg}$, MoF_6 , $\text{Ni}(\text{CO})_4$, $\text{Nb}(\text{OC}_2\text{H}_5)_6$, HReO_4 , $\text{Ta}(\text{OC}_2\text{H}_5)_5$, $\text{C}_5\text{H}_5\text{Tl}$, SnCl_4 , pi-allyl compounds of Group IIIa, IVa, Va, VIa, VIIa, or VIIIa metals, and combinations thereof, all of which can be converted into inorganic materials which resist diffusion.

The composites of the present invention can be prepared by the method which follows, to which the present invention also relates. A polymer which has free volume
20 therein is provided. The free volume is evacuated, and the evacuated free volume is infused with inorganic or organic molecules.

The free volume which is evacuated and into which the inorganic or organic molecules are infused can be natural free volumes (i.e., free volumes which are neither created nor modified by exposure of the polymer to supercritical fluids under supercritical
25 conditions prior to or during the evacuation or infusion).

Preferred inorganic molecules are those which can be converted into inorganic materials which are resistant to diffusion, such as inorganic molecules which can be polymerized into macromolecular networks or which can be treated so that the inorganic molecules interact with the polymer's functionality. Suitable inorganic molecules include
30 compounds and complexes of metal atoms (such as the alkali metals, the alkaline earths, the transition elements, the lanthanides, the actinides, boron, aluminum, gallium, indium, thallium, silicon, germanium, tin, lead, phosphorous, arsenic, antimony, bismuth, selenium, tellurium, polonium, and astatine, and, particularly in cases where they are bonded to other

atoms via non-covalent bonds (e.g., ionic bonds and pi-pi bonds), carbon, nitrogen, sulfur, and iodine), especially V, W, Fe, Ti, Si, Al, P, Sb, As, Ba, B, Cd, Ca, Ce, Cs, Cr, Co, Cu, Ga, Ge, In, Pb, Mg, Hg, Mo, Ni, Nb, Re, Ta, Tl, Sn, Ir, Rh, Th, Ru, Os, Pd, Pt, Zn, Au, Ag, combinations thereof, and their ions. The ligands to which the metal atom or ion is bonded or complexed is not particularly critical, though it is preferred that the ligand be chosen so that the inorganic molecule be labile through exposure to oxidizing, hydrolyzing, hydrogenating, chemical, or electrochemical environments, as well as being labile through exposure to heat or actinic radiation, such as ultraviolet radiation. Suitable ligands include those disclosed above. Specific examples of inorganic molecules which can be used in the practice of the present invention include VOCl_3 , $\text{W}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$, TiCl_4 , SiCl_4 , AlCl_3 , PCl_3 , SbCl_3 , $\text{As}(\text{C}_2\text{H}_5)_3$, $\text{Ba}(\text{C}_3\text{H}_7)_2$, borane pyridine and tetrahydrofuran complexes, $\text{Cd}(\text{BF}_4)_2$, $\text{Ca}(\text{OOCCH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9)_2$, cerium (III), 2-ethylhexanoate, cesium 2-ethylhexoxide, chromium (III) naphthenate, CrO_2Cl_2 , $\text{Co}(\text{CO})_3\text{NO}$, copper (II) dimethylaminoethoxide, triethylgallium, GeCl_4 , triethylindium, lead naphthenate, $\text{C}_2\text{H}_5\text{MgCl}$, $(\text{CH}_3)_2\text{Hg}$, MoF_6 , $\text{Ni}(\text{CO})_4$, $\text{Nb}(\text{OC}_2\text{H}_5)_5$, HReO_4 , $\text{Ta}(\text{OC}_2\text{H}_5)_5$, $\text{C}_5\text{H}_5\text{Tl}$, SnCl_4 , pi-allyl compounds of Group IIIa, IVa, Va, VIa, VIIa, or VIIIa metals, and combinations thereof.

Suitable organic molecules are those which can be converted into polymeric materials which are resistant to diffusion, such as macromolecular networks. Suitable organic molecules include compounds such as, acetylene, p-phenylene, thiophene, 2,5-thienylene, pyrrole, 2,5-pyrrolylene, 3-substituted 2,5-thienylene, 3-substituted pyrrole, aniline, p-phenyl-enevinylene, 2,5-pyridinediyl, hexadiyne, and diacetylenes. All of these compounds can be diffused into the polymer and then oxidatively, chemically, or photochemically converted to their corresponding macromolecular complex so that they form a non-diffusible macromolecular network within the free volume of the polymer. Since macromolecular networks made from these organic molecules can be electrically or ionically conducting, infusion of these organic molecules can add varying degrees of electrical and/or ionic properties to the composite material without significantly changing the crystallinity, flexibility, or Td of the starting polymer material. Aromatic organic molecules, such as naphthalenes and pyridines can also be infused to add optical properties to these materials. However, these aromatic materials cannot be polymerized into macromolecular networks and, therefore, are not as stable with respect to diffusion out of the polymer, except in cases where they can complex with the polymer matrix's functionality.

As indicated above, the free volume of the polymer is first evacuated. As used herein evacuating means reducing the pressure in the free volume of the polymer to less than atmospheric pressure (i.e., less than 760 Torr). This can be carried out by placing the polymer in a chamber, vessel, or other container capable of withstanding the vacuum being employed and reducing the pressure in the chamber, vessel, or other container to less than about 760 Torr, more preferably from about 100 Torr to about 10 mTorr or less, and most preferably from about 1 Torr to about 10 mTorr or less. Evacuation is typically achieved in from about 1 minute to about several days, depending on temperature and pressure.

The free volume, thus evacuated, is then infused with the inorganic or organic molecules. In contrast to the methods of the prior art, the infusion here is carried out under non-supercritical conditions (e.g., in the absence rather than in the presence of supercritical and carrier fluids, under conditions which do not produce created free volume and associated polymer swelling, and the like).

The infusion can be carried out by any practical method. Most conveniently, the infusion is carried out with the inorganic or organic molecule in a gaseous state by contacting the evacuated polymer with the gaseous inorganic or organic molecule. The inorganic or organic molecule can be naturally in the gaseous state, as is the case with some of the metal carbonyls, or the inorganic or organic molecules can be boiled, sublimed, or otherwise vaporized, such as with heat or under reduced pressure or both. In many cases the inorganic or organic molecules will be at least somewhat reactive with the air; in these cases, vaporization, as well as all other manipulations of the inorganic or organic molecules, are best conducted in an inert atmosphere, such as under argon or nitrogen, or in a vacuum.

The gaseous inorganic or organic molecule is then contacted with the evacuated polymer. This can be carried out by placing the polymer into a vessel, evacuating the vessel to a pressure less than 760 Torr, and then flowing the gaseous inorganic or organic molecules into the evacuated vessel containing the evacuated polymer. Infusion can be accelerated and, generally, more of the gaseous molecules can be infused by effecting the infusion process in a atmosphere of pure gaseous inorganic or organic molecules, preferably at elevated temperatures. The temperature and pressure at which the infusion is effected is important because they affect the time required for the infusion process. Temperature and pressure are preferably optimized within a range that allows the inorganic or organic

materials to have vapor pressures of greater than zero and increases the concentration of amorphous regions within the polymer (which provides for more free volume).

It is believed that, by initially evacuating the vessel holding the polymer, the rate of infusion of the inorganic or organic molecules is enhanced, because the inorganic or organic molecules do not need to displace ambient gases residing in the polymeric's free volume.

In a preferred embodiment of the present invention, infusion is carried out at temperatures greater than about 50 °C below that of the polymer's glass transition temperature ("Tg") and less than the thermal decomposition temperature ("Td") of the starting polymer material (i.e., at temperatures greater than about Tg - 50 °C but less than about Td). The greater the temperature, the greater the rate of incorporation of the inorganic or organic molecules infused into the polymer. Also, the greater the temperature, the greater the resulting concentration of inorganic or organic material diffused into the polymer due to thermal rearrangement which acts to increase the free volume within the polymer. It is to be understood that these are only preferred conditions and that the same processes can be carried out outside of these preferred temperature ranges. In some cases, effecting infusion outside this temperature range may be preferred, such as to control the concentration of the inorganic or organic molecules in the finished composite. As the skilled practitioner will note, in order to practice the present invention in the preferred temperature range, the inorganic or organic molecule must have a non-zero vapor pressure at temperatures greater than about Tg - 50 °C but less than about Td of the polymer and/or at the pressure used during the infusion process. In some cases, heating the polymer to temperatures which optimize free volume space may result in thermal decomposition of the inorganic or organic molecules one wishes to infuse into the polymer. In such cases, infusion is best carried out at temperatures and pressures at which the inorganic or organic molecules can achieve a vapor pressure of greater than zero but not thermally decompose. As indicated above, the time required for infusion varies depending on the temperature, the pressure, the nature of the inorganic or organic molecules, the nature of the polymer, the desired degree of infusion, the desired concentration of inorganic or organic molecules, and the like. In most circumstances, infusion can be effected in from about a few minutes to about 2 days.

After infusing the inorganic or organic molecules into the polymer, the inorganic or organic molecules can be polymerized under conditions effective to cause the inorganic

or organic molecules to assemble into macromolecular networks. Preferably, the polymerization is carried out in the absence of free (i.e., non-infused) inorganic or organic molecules. Consequently, it is preferred that, prior to polymerization, the infused polymer be removed from the atmosphere containing gaseous inorganic or organic molecules or that
5 the atmosphere surrounding the infused polymer be evacuated or replaced with an inert gas.

Polymerization can be carried out by exposing the inorganic or organic molecules infused in the free volume of the polymer to any suitable polymerizing condition. For example, the infused inorganic or organic material can be oxidized, hydrolyzed, hydrogenated, chemically treated, photoactivated, electrochemically polymerized, or
10 thermally polymerized by exposing the infused inorganic or organic material to appropriate conditions, such as by exposing the infused inorganic or organic material to an oxidizing agent, a hydrolyzing agent, a hydrogenating agent, a specific chemical (e.g. electrochemical or photochemical), actinic radiation, suitable voltages, or appropriate temperatures.

Typically, the oxidizing, hydrolyzing, or hydrogenating agent is gaseous or is
15 contained in vapor form in an inert gas. For convenience, oxidation or hydrolysis can be effected by exposing the inorganic molecules to a gas which includes water, oxygen or combinations thereof, such as ambient air. The oxidation, hydrolysis, or hydrogenation can be carried out at any convenient temperature or pressure, preferably at room temperature and ambient pressure and at temperatures below the polymer's T_d and the inorganic or
20 organic molecules decomposition temperature. In the case where the inorganic or organic molecules are air or moisture sensitive, oxidation or hydrolysis can be conveniently carried out at ambient pressure and temperature and in ambient air in from about 5 min to about 48 hours.

Hydrogenation can be carried out by exposing the infused polymer to hydrogen
25 gas. For example, a polymer containing a metal pi-allyl compound can be placed in an atmosphere of hydrogen gas at room temperature for from about 5 minutes to about 48 hours. The pi-allyl compound is reduced, propane gas is released, and a stabilized metal species or a metal network is formed in the free volume of the polymer. In the case where a metal network is formed in the polymer's free volume, the metal network may or may
30 not interact with functionalities contained within the polymer.

In some cases polymerization can be carried out chemically. For example, organic molecules of pyrrole can be infused into the polymer's free volume and then converted to polypyrrole by contacting the polymer material with a chemical solution containing 50%

water and 50% HNO_3 . This solution oxidizes the pyrrole to a macromolecular network of polypyrrole which resides throughout the free volume of the polymer. Alternatively, the polymer can be first converted to a composite as described herein such that the macromolecular network contained in the polymer has oxidative properties. One suitable
5 macromolecular network having oxidative properties is V_2O_5 . After formation of this composite containing V_2O_5 , organic molecules like pyrrole can be infused, which then are oxidized by the V_2O_5 macromolecular network to form a macromolecular polypyrrole network within the polymer's free volume.

Organic monomers which can be electrochemically polymerized, such as acetylene
10 or thiophene, once infused into the free volume of the polymer, can be polymerized by contacting the infused polymer with an electrode and adjusting the potential of the electrode to facilitate oxidative polymerization of the organic molecules.

As a further example, thermal treatment of the organic molecule $\text{C}_6\text{H}_4\text{-CH}_2\text{-(R}_2\text{-S}^+\text{X}^-)\text{-CH}_2\text{-}$ facilitates polymerization to the macromolecular polymer
15 polyphenylenevinylene. (See, for example, Yamamoto, which is hereby incorporated by reference.)

Once polymerized, the inorganic or organic molecules self-assemble into macromolecular networks over a period of time ranging from simultaneous assembly upon exposure to the polymerizing conditions to a few hours to a few days.

The assembled macromolecular network can, optionally, be infused with dopants, such as Na, I_2 , Br_2 , FeCl_3 , AlCl_3 , AsF_5 , and those disclosed in Yamamoto, which is hereby incorporated by reference, to enhance the conductive properties of the macromolecular network contained within the free volume of the polymer. Further description of these
20 processes and their utility in making, for example, polymeric batteries, electrolytic capacitors, electrochromic devices, diodes, solar cells, and non-linear optic materials, can be found in Yamamoto, which is hereby incorporated by reference.

It is believed that, because the inorganic or organic molecules which are diffused into the polymer are confined to the polymer's free volume, the resulting self-assembled macromolecular networks are mainly limited to extending lengthwise (i.e., only a
30 monolayer to a few layers of the network can form in two dimensions and the growth of the network is mainly through a one dimensional extension of a single monolayer chain through the interconnected free volumes contained within the polymer). It is further believed that this results in a material whose polymer phase is relatively unchanged with

respect to flexibility, crystallinity, Td, and other physical properties. In essence, the polymer is believed to act only as a molecular template into which the inorganic network is formed along the free volume space associated with these materials. However, since the inorganic or organic macromolecular network is contained in free volumes which are
5 homogeneously incorporated throughout the polymer, it imparts its own properties to the composite as a whole. Such imparted properties include controlled and varying optical densities, catalytic properties, and electrical and ionic conductivities, as well as enhanced thermal-mechanical properties.

Alternatively, particularly in cases where the polymer contains a suitable
10 functionality, the infused inorganic or organic molecules can be treated under conditions effective to cause the inorganic or organic molecules to interact with the polymer's functionality. As described above, suitable polymer functionalities include halogens (such as fluorines or chlorines), amines, alkenes, alkynes, carbonyls (such as keto groups, aldehyde groups, carboxylic acid groups, ester groups, amide groups, and the like),
15 alcohols, and thiols. Inorganic molecules which are interacted with functionalities on the polymer can have the formula M^yX_j , where X is a functionality contained within the polymer (e.g., halogen, such as F or Cl, NH_2 , NH, O-C=O, C-OH, C=C, C≡C, or C=O), y is the oxidation state of the metal, which can range from zero to the highest oxidation state of the particular metal, and j is the number of ligands to which the particular metal can
20 ligate within a given polymer. For example, where M is Pd, and X is Cl, j can be 2. In cases where the inorganic or organic molecules contain metal atoms or ions, the interacted metal and polymer functionality can generally be characterized as an inorganic complex, although other types of interactions, such as covalent interactions, ionic interactions, pi-pi electronic interactions, and the like are also contemplated.

25 The interaction between the inorganic or organic material can be spontaneous, i.e., it can occur immediately or over a period of time simply by virtue of the inorganic or organic material being in close proximity with the polymer's functionality. In this case, treating simply means permitting the inorganic or organic molecules to interact with the polymer's functionality. In other cases, the interaction between the inorganic or organic
30 material is not spontaneous and requires that the inorganic or organic molecules be actively treated, such as by oxidizing, hydrolyzing, hydrogenating, chemically treating, or photoactivating, electrochemically activating, the infused inorganic or organic molecules. The oxidized, hydrolyzed, hydrogenated, chemically treated, photoactivated,

electrochemically activated inorganic or organic molecules then go on to interact with the functionality of the polymer. In practicing this aspect of the present invention, oxidizing, hydrolyzing, hydrogenating, chemically treating, or photoactivating, electrochemically activating the infused inorganic or organic molecules can be carried out by the methods
5 described above in regard to polymerizing the inorganic or organic molecules.

In some cases, most notably in the cases where the inorganic molecules contain metal atoms and ligands bonded thereto where the metal ligand bond strength is large, oxidation, hydrolysis, or hydrogenation of the ligands may be slow or incomplete. For comparisons of metal ligand bond strength and the tendency for metals to hydrolyze see
10 Huheey, Inorganic Chemistry, 3rd Edition. Principles of structure and reactivity, New York:Harper and Row, Chapters 7 and 11, which is hereby incorporated by reference. In these cases, it is advantageous to expose the inorganic molecules to actinic radiation, such as ultraviolet ("UV") radiation, preferably a broad band source of about 190 nm to about 400 nm, (or, in some cases, high energy UV (e.g., wavelengths less than 190 nm) or x-
15 radiation), under conditions effective to cleave the ligands from the metal atoms, typically for a period of time related to the strength of the metal ligand bond and the power output (i.e., power density) of the radiation source.

The metal atoms having the ligands cleaved therefrom can be treated photochemically, chemically, electrochemically, or thermally under conditions effective to
20 cause the metal atoms to interact with the polymer's functionality.

Alternatively, the metal atoms having the ligands cleaved therefrom can then be exposed to an oxygen or water containing gas under conditions effective to cause the metal atoms to assemble into macromolecular networks. An oxygen or water containing gas or atmosphere is preferably present while exposing the inorganic molecules (diffused into the
25 polymer) to actinic radiation, so that oxidation or hydrolysis can occur immediately upon cleavage of the ligand from the metal. Oxygen or water containing gases suitable for use in this process include: substantially pure oxygen; oxygen mixed with water and/or an inert gas, like Ar or N₂; or ambient air.

For example, W(CO)₆ is a tungsten metal complex which contains 6 carbonyl
30 ligands. The carbonyl ligands are labile to heat or UV radiation. However, their lability decreases with the loss of each carbonyl ligand. In other words, upon loss of the first carbonyl, the second carbonyl becomes more difficult to remove; upon loss of the second carbonyl, the third carbonyl becomes more difficult to remove; and so on. Thus, after

infusion of $W(CO)_6$ into a polymer, loss of the carbonyl ligands is preferably carried out by activating the tungsten-carbonyl bond by exposure to a broad band ultraviolet source (e.g., radiation between 190 nm and 400 nm) to facilitate the total decomposition of the $W(CO)_6$. The decomposed tungsten complex is then free to interact with the polymer's
5 functionality or to react with neighboring decomposed tungsten complexes to form a macromolecular tungsten oxide network.

It is believed that the forgoing polymerization of the inorganic or organic molecules and assembly into macromolecular networks and/or the foregoing treatment of the inorganic or organic molecules to cause their interaction with the polymer's
10 functionality results in improved stability of the complex, such as, for example, by reducing migration of the inorganic or organic molecules out of the free volume of the polymer.

The composites of the present invention are useful, for example, in the construction of lightweight, flexible, electromagnetic, UV and x-radiation shields; flexible components for use in the construction of electrochromic or liquid crystal based flat panel
15 displays; and electrode and separator materials used in the construction of lightweight, high energy density batteries.

The composites of the present invention and composites produced in accordance with the method of the present invention, particularly those containing vanadium and oxygen, such as vanadium pentoxide, can be used as an electrically-conductive imaging
20 layer of an electroconductive imaging element, such as those which are employed in high speed laser printing processes. The electroconductive imaging element typically includes an insulating support, an electrically-conductive layer overlaying the support, and a dielectric imaging layer overlaying the electrically-conductive layer. Further details regarding the construction and use of these electroconductive imaging elements can be
25 found, for example, in Anderson I, which is hereby incorporated by reference.

The composites of the present invention and the composites made by the processes of the present invention, particularly those containing a vanadium oxide macromolecular network, can be used as antistatic materials in photographic elements, such as photographic films and papers. These photographic elements include a substrate, one or more light
30 sensitive layers, and one or more anti-static layers containing the composite of the present invention. Other component layers, such as subbing layers, barrier layers, filter layers and the like can also be employed. A detailed description of photographic elements and their

various layers and addenda can be found in, for example, James, The Theory of the Photographic Process, 4th ed. (1977), which is hereby incorporated by reference.

The present invention is also directed to a fuel cell, such as a battery. The fuel cell includes a composite of the present invention or a composite produced in accordance with the method of the present invention, particularly those that are electrically or ionically conductive. The fuel cell further includes an anode and a cathode which are in contact with the composite.

The present invention is also directed to a method for shielding a material from electromagnetic radiation emitted from an electromagnetic radiation source. The method includes disposing a composite of the present invention or a composite produced in accordance with the method of the present invention between the material to be shielded and the electromagnetic radiation source. Composites whose inorganic or organic molecules include a metal complex, such as iron, titanium, and vanadium complexes, are particularly well suited for shielding visible and ultraviolet radiation. Composites whose inorganic or organic molecules include a metal having a high Z number, such as tungsten lead, and gold, also shield high-energy ultraviolet light and x-rays. As used herein, shielding is meant to include filtering, such as when the intensity of the electromagnetic radiation is partially reduced (e.g., by 50% or more), as well as blocking, such as when the electromagnetic radiation is completely absorbed or reflected by the composite.

The composites of the present invention can also be used as a flame or heat retardant material. More particularly, composites which contain a zinc oxide, a zinc/molybdenum oxide, a zinc/chromium oxide, a zinc/silicon oxide, a zinc/titanium oxide, a bismuth/boron oxide, a molybdenum/tin oxide, a molybdenum oxide, an antimony oxide, alumina, or silica macromolecular network or combinations thereof can be used in place of the fluoropolymer composition described in U.S. Patent No. 4,957,961 to Chandrasekaren et al., which is hereby incorporated by reference, to thermally insulate wires and jacketing cables and to protect them from flames and smoke. Accordingly, the present invention is also directed to a method for shielding a material from heat or flame. The method includes disposing a composite of the present invention or a composite produced in accordance with the method of the present invention between the material to be shielded and the source of heat or flame. As used herein, the heat or flame source can be an actual heat or flame source or a potential heat or flame source.

In addition, the composites of the present invention which contain inorganic metallic networks known to be useful conventionally as catalysts for carrying out molecular transformations can be used for heterogeneous catalysis of, for example, flue gasses, car emissions, precursors to commercially valuable industrial grade and fine chemicals, and the like. The composites of the present invention are equally useful in batch as well as in continuous flow processes.

Catalyzing a reaction of a reactant using the composite of the present invention involves first providing a composite of the present invention wherein the inorganic material is suitable for catalyzing the reaction of the reactant and then contacting the composite with the reactant. Inorganic materials suitable for catalyzing reaction of particular reactants can be identified simply on the basis of known conventional catalysts for the particular reactant. For example, vanadium containing compounds, such as vanadium pentoxide, a well known conventional catalyst for the reaction of SO_2 to SO_3 with molecular oxygen, can be used as the inorganic material in the composite of the present invention to catalyze that reaction. Optimum reaction conditions for use of the composites of the present invention can be worked out for each individual reactant and inorganic material by methods well known in the art. Some reactions in which the composites of the present invention can serve as effective catalysts and procedures and apparatus suitable for carrying out catalysis using the present composites include those described in Patchornick et al., J. Chem. Soc., Chem. Commun., 1990:1090 (1990) ("Patchornick"), U.S. Patent 5,534,472 to Winslow et al. ("Winslow"), and U.S. Patent 5,420,313 to Cunningham ("Cunnington") et al., which are hereby incorporated by reference.

Illustrative reactions which can be catalyzed with appropriate choice of inorganic or organic macromolecular network include: conversion of alkenes to epoxides using late transition metal complexes; conversion of alkenes to aldehydes using early transition metals such as titanium; selective oxidation of alcohols to aldehydes using late transition metals. Again, the efficiency of these and other reactions can be tuned by proper choice of metal and coordination environment, e.g., the surrounding ligands and steric encumbrance of the surrounding polymer.

As indicated above, transition metals, are particularly useful metals for incorporation into the composites of the present invention when these composites are to be used as catalysts. The unique characteristics of each transition metal for catalyzing different kinds of synthetic reactions should be considered. For example Fischer-Tropsch

synthesis ("FTS") of hydrocarbons was stimulated in 1974, when the oil supply crisis relied heavily on the hydrogenation of CO to CH₄. The pattern of transition metals within the transition metal periods of the Periodic Table shows varying activities of these metals. A description of various transition metals and their utility for FTS is given in, for example, 5 "Studies in Surface Science and Catalysis," vol. 79 in Moulijn et al., eds, Catalysis. An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysts, Elsevier Science Publishers B.V. (1993) ("Moulijn"), which is hereby incorporated by reference. As a further example, the catalytic oxidation of sulphur dioxide and ammonia to produce sulfuric acid and nitric acid, respectively, are extremely important industrially based 10 processes. Oxidative catalysis of ethylene and propylene epoxides and phthalic anhydrides among others are also examples of relevant industrially based catalytic conversions of alkanes by oxidative catalysis. An illustrative list of oxidative catalytic based syntheses of important industrial materials which can be catalyzed with the composites of the present invention is provided in Moulijn at p. 187, which is hereby incorporated by reference.

15 For example, the present invention can be used to catalyze the oxidation of an oxidizable substrate. Suitable oxidizable substrates include substituted or unsubstituted alkyl or arylalkyl alcohols, such as methanol (in which case the resulting product of oxidation is formaldehyde or formic acid or both), or a substituted or unsubstituted alkyl or arylalkyl, such as o-xylene (in which case the product of oxidation is phthalic anhydride, a 20 precursor useful in the preparation of many polymers).

The reaction is carried out by contacting the oxidizable substrate with the oxidizing agent in the presence of a composite of the present invention or a composite prepared in accordance with the method of the present invention. Any suitable oxidizing agent can be employed. Preferably the oxidizing agent is a gas, such as oxygen gas (O₂), 25 optionally mixed with an inert gas, such as helium, nitrogen, or argon. In many cases, ambient air can be used as the oxidizing agent. The composite employed can be of any suitable form, for example, sheets, beads, fibers, powders, and the like. Preferably, the composite's polymer is a fluoropolymer (e.g., MFA, PFA, PVDF, PTFE, ECTFE, or FEP). Composites which include a titanium- or vanadium-containing inorganic material disposed 30 in the polymer's natural free volume are particularly useful to catalyze the present invention's oxidation reactions. In some cases, the oxidation reactions can be advantageously carried out in the presence of a co-reductant. Examples of suitable co-reductants include iodosobenzene, which is commonly used in the epoxidation of olefins in

the presence of metalloporphyrins, and peroxides (e.g., hydrogen peroxide or benzoyl peroxide).

In many cases, it is desirable to swell the composite of the present invention during or before its use as a catalyst to increase the rate of diffusion of reactant into the composite. This can be carried out by exposing the composite to standard supercritical conditions. For example, the composite can be placed in a vessel capable of withstanding high pressures, such as the pressures commonly encountered in supercritical catalytic processes. The vessel is then charged with a supercritical fluid under supercritical conditions, such as carbon dioxide at 2500 psi, and the pressure is maintained for a period of time ranging from 1 to 100 hours. As a result of being exposed to these supercritical conditions, the composite swells. However, in contrast to the materials of the prior art in which impregnation is carried out under supercritical conditions, the inorganic or organic materials infused in accordance with the methods of the present invention do not diffuse out of the polymer upon the composite's subsequent exposure to supercritical conditions.

The effectiveness of the composites of the present invention as heterogeneous catalysts is believed to be due to the residence of the inorganic material along the polymer structure that is at the surface of free volume and which is accessible to the gas phase molecules to be catalytically transformed. This is in contrast to conventional inorganic-organic blends where the mixing and blending procedures fail to control placement of the inorganic phase and where, in view of the surface free energy constraints, it is believed that mixing and curing procedures would likely lead to materials which would have little if any inorganic material at the surface of the free volume.

The present invention also relates to a method for preventing fouling of a surface by organisms. In marine (i.e., salt water) or aquatic (i.e., fresh water) environments, surfaces which are in continuous or intermittent contact with these environments are frequently subject to fouling, such as by attachment or growth of organisms on the surfaces. In one method of the present invention, fouling of the surface is prevented by applying, to the surface, a composite of the present invention or a composite made in accordance with the method of the present invention.

For example, fouling of a surface is prevented in accordance with the present invention by applying, to the surface, a composite comprising a polymer having free volume therein and an inorganic or organic material disposed in the free volume of the

polymer. Free volume, as explained above, includes natural free volume, created free volume, or both.

The composite can be applied to the surface by any suitable method. For example, in one embodiment, the composite can be provided in sheet (i.e., relatively planar) form. The sheet can then be contacted with the surface under conditions effective to attach the sheet to the surface. Illustratively, the sheet can be attached mechanically (e.g., by nailing, screwing, or riveting) or by adhering the sheet to the surface (e.g., by gluing or epoxying). In an alternative embodiment, the composite can be provided in bead or powder form dispersed in an uncured resin. Suitable resins include those that can be cured by polymerization or cross-linking. The composite in bead or powder form dispersed in the uncured resin is contacted with the surface, such as by painting (e.g., brushing or rolling), spraying, sputtering, or dipping. The uncured resin is then cured, such as by exposure to light or heat. The curing process can be taken to completion, but should, at a minimum, be carried out to a degree that is effective to attach to composite beads or powder to the surface. Still alternatively, uncured resin can be applied to the surface, such as by painting (e.g., brushing or rolling), spraying, dipping, or sputtering, and then contacting the composite bead or powder with the uncured resin. The resin is then cured to a degree which is effective to attach the composite beads or powder to the surface. In another embodiment, the composite can be provided in bead or powder form dispersed in a suitable solvent (e.g., ketones, ethers, hydrocarbons (e.g., unsubstituted hydrocarbons or chlorinated hydrocarbons), and aromatic solvents (e.g., benzene, toluene, or xylenes)). As used here, "dispersed" is meant to include "dissolved". The composite beads or powders dispersed in suitable solvent is then contacted with the surface, such as by painting (e.g., brushing or rolling), spraying, dipping, or sputtering, and the solvent is evaporated, such as by heating the surface or by simply permitting the solvent to evaporate at room temperature. In yet another embodiment, the composite in bead or powder form can be applied neat with a coating method which directly applies films or coatings of the beads or powders via thermally based spraying, sputtering, or dipping or via use of high-temperature plasma spray technology.

In some situations, it can be advantageous to separate the surface being protected from the composite so that the composite's catalytic activity does not cause the surface to degrade. For example, where the surface being protected from organism fouling is a metal surface, it may be advantageous to first coat a barrier layer prior to applying the composite

of the present invention. Such barrier layers can be made of a non-reactive metal or, preferably, a polymer.

Where the surface to be protected from organism fouling is the polymer surface of a polymer having free volume therein, an alternative method of the present invention can be employed. In this method, the polymer's free volume is evacuated, and inorganic or organic molecules are infused into the evacuated free volume of the polymer. This method is particularly suitable where the surface is the surface of a polymer object, such as a plastic pipe or a hull of a fiberglass boat or canoe. However, the method can be employed to prevent organism fouling of surfaces made of metal or other non-polymeric objects by first disposing a polymer having a free volume on the object's surface and then evacuating the polymer's free volume and infusing inorganic or organic molecules into the evacuated free volume. By adjusting the duration of the infusing step, one skilled in the art can readily infuse only the portion of the polymer proximate to the polymer's exposed surface, thus, in effect, producing a barrier layer which prevents the catalytic activity of the infused materials from degrading the object's metal or other non-polymeric surface. Suitable methods for evacuating and infusing polymeric materials include those discussed above with regard to making the composites of the present invention.

Although the mechanism by which fouling is prevented in the above methods is not fully understood, it is believed that the inorganic or organic material contained in the polymer's free volume either directly inhibits the growth of organisms on the composite surface or indirectly catalyzes an unidentified reactant at the composite surface which resists fouling via organism attachment or growth. For example, where the inorganic or organic material is an inorganic material containing vanadium, titanium, or other metal capable of catalytically splitting dioxygen (i.e., O_2), it is hypothesized that any organism that is aerobic (i.e., requires dioxygen for respiration) will not thrive or proliferate at such a surface, because the organism's respiratory cycle will be disrupted by the intake of the oxygen radical species created when the metal (e.g., vanadium or titanium) splits the dioxygen. Therefore, it is envisioned that composites containing metals capable of splitting dioxygen, such as vanadium, would be particularly effective, especially against fouling by aerobic organisms. Using this method, fouling by marine organisms, aquatic organisms, and microorganisms (e.g., bacteria, protozoa, algae, and the like) is prevented or reduced. Since crustaceans (particularly barnacles) and mussels (particularly zebra mussels) are especially devastating to aquatic and marine surfaces, it is expected that the method of the

present invention will find particular utility in preventing fouling of these surfaces by crustaceans or mussels.

The method of the present invention can be used to prevent organism fouling of a variety of surfaces, including those of water-going vessels (e.g., boats, ships, barges, and canoes), components of such water-going vessels (e.g., hulls, propellers, anchors, and anchor chains), and stationary objects that are in contact with aquatic or marine environments (e.g., piers, buoys, underwater components of bridges, oil rigs, and drilling platforms, lock gates and associated components, pipes, and underwater cables).

When the composites of the present invention are used to prevent fouling of surfaces by organisms, it is preferred that the polymer be a fluoropolymer, because fluoropolymer surfaces have low coefficients of friction and are inherently non-stick and hydrophobic. Moreover, as explained above, it is believed that the catalytic properties of the present invention's composites are enhanced when fluoropolymers constitute the polymer. Thus, the enhanced catalytic activity provided by the fluoropolymer, coupled the non-stick character of the fluoropolymer surface, makes a surface that has enhanced resistance to organism proliferation and is easy to clean. In cases where the composite of the present invention is used as an anti-fouling coating on water-going vessels, the fluoropolymer's low coefficient of friction also reduces the drag experienced by such vessels.

The antifouling method of the present invention is particularly advantageous in environments which are sensitive to the toxic effects of heavy metals. Conventional antifouling marine coatings generally include toxic materials (e.g., copper or tin). These conventional coatings operate primarily when the toxic materials are ingested by marine organisms which, because of the toxic material's effect, subsequently die. The ingestion process can take place either by ingestion via direct contact of the organism with the coating or via ingestion of toxic material which has leached from the antifouling coating into the environment. In the antifouling method of the present invention, it is believed that no toxic material is deposited into the environment. Furthermore, because the composites of the present invention do not operate by releasing the active ingredient (e.g., metal), it is expected that the composite will have a much greater antifouling lifetime. This is especially important in applications which require that the surface be underwater for extended periods of time (e.g., underwater components of bridges and oil rigs, piers, hulls of large ships, or underwater pipes or cables).

The present invention also relates to objects having a surface. All or a portion of the surface includes a polymer which has free volume therein, and, in the free volume of the polymer, is disposed an inorganic or organic material. Suitable objects include those which are in continuous or intermittent contact with water and, therefore, which are particularly susceptible to fouling by organisms. Other suitable objects are those which are exposed to damp and/or humid environments.

For example, the object can be a water-going vessel which comprises a hull having attached thereto, on at least a portion of the hull's exterior surface, a composite according to the present invention. As used herein, hull is meant to include all portions of a ship, boat, barge, or other water-going vessel below the deck line, including those portions which are typically below the waterline, as well as those portions which are typically above the waterline but which intermittently come into contact with water. Also included within the meaning of hull, as used herein, are those portions of the water-going vessel that are in contact with the hull, such as propellers, anchors, anchor chains, piping, cables, and the like.

Another suitable object in accordance with the present invention is a pipe. The pipe includes a pipe wall having an interior surface and an exterior surface and, in addition, a composite according to the present invention attached to at least a portion of the pipe's interior surface, exterior surface, or both. For example, in cases where the pipe is to be used for transmission of fresh or salt water, the pipe should have its interior surface, or a portion thereof, coated with the composite. In cases where the pipe is to be used underwater, the composite should be attached to the pipe's exterior surface. In certain circumstances, such as where the pipe transmits water to or from an underwater location (e.g., intake or discharge pipes used in power plant cooling operations), a pipe having the composite attached to its interior and exterior surfaces would be preferred. Water intake pipes for domestic or municipal water treatment facilities are frequently plagued by the accumulation of organisms (particularly, zebra mussels) at the pipe's inlet. In such situations, a pipe having the composite of a present invention disposed at the intake portion thereof would be advantageous.

Stationary structures having supports, the surface of which supports are in continuous or intermittent contact with water, are also envisioned as suitable objects. A composite of the present invention is attached to at least a portion of the support's surface.

Stationary structures, as used herein, include drilling platforms, oil production rigs, bridges, and piers.

The water-going vessels, pipes, and structures of the present invention can be prepared using the above-described methods for applying the composite of the present invention to surfaces. In cases where the water-going vessels, pipes, or structures have polymer surfaces which include a polymer having free volume therein, the water-going vessel, pipe, or structures of the present invention can be prepared by evacuating the polymer's free volume and infusing inorganic or organic molecules into the free volume, as described above.

Although the antifouling coatings described above have been illustrated in terms of pipes, water-going vessels, and structures they can be used on all types of surfaces that are exposed to water, such as stagnant water, damp or humid conditions, or other environments conducive to the growth of marine, aquatic, or microorganisms. Examples of such surfaces include sinks, swimming pool liners, countertops, pond liners, roofing materials, dish pans, flooring, and concrete surfaces. Because medical devices and equipment (e.g., catheters or temporary or permanent in vivo mechanical devices) are frequently exposed to environments which promote microbial growth, applying the composites of the present invention to the surfaces of these devices and equipment is contemplated.

The present invention, in another aspect thereof, relates to oxyhalopolymer composites and surface-oxyhalogenated non-halopolymer composites.

As used herein, oxyhalopolymers refer to halopolymer bulk materials whose surface is modified with hydrogen atoms and oxygen atoms or oxygen-containing radicals.

As used herein oxyhalopolymer composites refer to oxyhalopolymers in whose free volume is disposed an inorganic or organic material.

As used herein, halopolymers refer to halopolymer bulk materials, which have surface halogen atoms.

As used herein, halopolymer composites refer to halopolymers in whose free volume is disposed an inorganic or organic material.

As used herein, non-halopolymers refer to polymeric bulk materials other than halopolymers.

As used herein, non-halopolymer composites refer to non-halopolymers in whose free volume is disposed an inorganic or organic material.

As used herein, surface-halogenated non-halopolymers refer to non-halopolymers whose surface is modified with molecularly bonded halogen atoms or a halocarbon or halohydrocarbon film. The outer surface of the surface-halogenated non-halopolymers thus has surface halogen atoms.

5 As used herein, surface-halogenated non-halopolymer composites refer to surface-halogenated non-halopolymers in whose free volume is disposed an inorganic or organic material.

As used herein, surface-oxyhalogenated non-halopolymers refer to surface-halogenated non-halopolymers whose molecularly bonded surface halogen atoms or
10 halocarbon or halohydrocarbon film's surface halogen atoms are modified with hydrogen atoms and oxygen atoms or oxygen-containing radicals.

As used herein, surface-oxyhalogenated non-halopolymer composites refer to surface-oxyhalogenated non-halopolymers in whose free volume is disposed an inorganic or organic material.

15 As used herein, polymers refer to one or more of the above halopolymers, non-halopolymers, oxyhalopolymers, surface-halogenated non-halopolymers, surface-oxyhalogenated non-halopolymers.

As used herein, polymer composites refer to one or more of the above halopolymer composites, non-halopolymer composites, oxyhalopolymer composites,
20 surface-halogenated non-halopolymer composites, and surface-oxyhalogenated non-halopolymer composites.

The present invention relates to an oxyhalopolymer composite. The oxyhalopolymer composite includes an oxyhalopolymer having free volume therein and an inorganic or organic material disposed in the free volume of the oxyhalopolymer.

25 The present invention also relates to a surface-oxyhalogenated non-halopolymer composite. The composite includes a surface-oxyhalogenated non-halopolymer which has free volume therein. The surface-oxyhalogenated non-halopolymer composite further includes an inorganic or organic material disposed in the free volume of the surface-oxyhalogenated non-halopolymer.

30 The oxyhalopolymer can be an organic based halopolymer or an inorganic-organic hybrid halopolymer. Organic based halopolymers suitable for use in the composites of the present invention can be homopolymers, copolymers, multicomponent polymers, or combinations thereof, so long as at least some of the homopolymers, copolymers,

multicomponent polymers, or combinations thereof contains halopolymer. Examples of suitable halopolymers as well as methods for their obtaining or making such halopolymers include those described above with regard to composites of the present invention.

Non-halopolymers suitable for use in the practice of the present invention include
5 organic based non-halopolymers or inorganic-organic hybrid non-halopolymers. Organic based non-halopolymers can be homopolymers, copolymers, multicomponent polymers, or combinations thereof, so long as they contain no significant amounts of halopolymer. That is, the non-halopolymer can include halopolymers, but only in amounts insufficient to render the non-halopolymer's chemical and physical properties closer to those of a pure
10 halopolymer than to those of a pure non-halopolymer. Suitable organic non-halopolymers as well as methods for their obtaining or making these materials include those described above in regards to the composites of the present invention.

The halopolymer and non-halopolymer can, alternatively, be an inorganic-organic hybrid polymer or blend of organic polymer and inorganic-organic hybrid polymer, such as
15 the ones described above. They can contain a variety of materials which are known in the art to modify the properties of the polymer, and they can be used in any suitable form. Exemplary property-modifying materials and suitable forms include those described above in conjunction with the present invention's composites.

The materials which make up the polymer (i.e., the halopolymer, the
20 oxyhalopolymer, the non-halopolymer, the surface-halogenated non-halopolymer, or the surface-oxyhalogenated non-halopolymer), be they an organic polymer or an inorganic-organic hybrid material, contain free volume (e.g., natural free volume or created free volume).

In addition to having free volume therein, the polymer used in the method of the
25 present invention also has a halogenated surface. In the case where the polymer is a halopolymer, the halopolymer will naturally have a halogenated surface (i.e., a surface with exposed surface halogen atoms). In the case where the polymer is a non-halopolymer, the surface can contain molecularly bonded halogen atoms (i.e., halogen atoms bonded directly to the carbon backbone of the non-halopolymer at the non-halopolymer's surface), or,
30 alternatively, the surface can be modified with a halocarbon or halohydrocarbon film. The thickness of the film is not critical to the practice of the present invention and can range from several microns to several inches, depending on the size of the non-halopolymer on which it is coated and the application to which it is to be put. Preferred halocarbon and

halohydrocarbon films are those which are polymeric in nature, for example, which are made of the halopolymers set forth above.

As indicated above, a portion of the surface halogen atoms of the oxyhalopolymer composites and surface-oxyhalogenated non-halopolymer composites of the present invention are substituted with hydrogen atoms and oxygen atoms or oxygen-containing radicals. In this regard, the objective is to have either oxygen or oxygen-containing groups disposed on the halopolymer or on the non-halopolymer's halogenated or halocarbon or halohydrocarbon surface in place of some of the halogen atoms to form a stable intermediate material. Generally, the oxygen atoms are not directly bonded into the polymer backbone per se (e.g., to form a C-O-C backbone), but only substitute for existing halogen atoms which are pendent on the carbon backbone. Representative oxygen-containing radicals suitable for use in the composites of the present invention include hydroxyl (-OH), ether (C-O-C), epoxide (-O-), aldehyde (-CHO), ester (-C(O)O-), and carboxylic acid (-COOH). Other suitable oxygen-containing radicals include oxo, alkoxy (e.g., methoxy, ethoxy and propoxy), radicals having the formula R'-CO- where R' is hydrogen or alkyl (particularly C1 to C5 lower alkyl, e.g., methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, isopentyl, neopentyl, and the like), and combinations thereof. In addition, the oxygen-containing radicals can also take the form of PO_y or SiO_{y'}, where y and y' are 2-3. Mixtures of oxygen and one or more oxygen-containing radicals and mixtures of two or more oxygen-containing radicals can also be present on the surface. In general, the oxygen sites on the surface of a halopolymer or a surface halogenated non-halopolymer need only be of such concentration that the oxygen functionality and resulting backbone of the polymer be stable. Typically, from about 1 to about 98%, preferably from about 3 to about 70 % of the original surface halogen atoms on the halopolymer or surface halogenated non-halopolymer are substituted with oxygen or oxygen-containing groups.

Oxyfluoropolymers, when produced by radio frequency glow discharge ("RFGD"), exhibit a wide variety of surface free energy increases where, for example, a fluoropolymer like PTFE with a γ_c of about 18 dynes/cm at 20°C can be increased to about 40 dynes/cm to a depth of between about 10 to about 100 Å for increased wettability and other surface properties relating to the surface free energy of a material. Even with such increases in surface free energy the hydrophobic properties of the original material are not destroyed. That is, the composites of the

present invention, having hydrogen, oxygen, and fluoride functionalities that are covalently bonded to the carbon polymer backbone, still may inhibit surface fouling, permeation, and wetting by liquids with high surface tensions (e.g., having surface tensions greater than about 50 dynes/cm), such as water and other similar polar solvents, while being wettable by liquids having low surface tensions (e.g., surface tensions less than 50 dynes/cm), such as blood plasma and other nonpolar organic solvents.

As indicated above, the oxyhalopolymer composite and surface-oxyhalogenated non-halopolymer composite of the present invention further includes an inorganic or organic material which is disposed in the polymer's free volume, preferably in the polymer's natural free volume. Details regarding the amount, physical and chemical characteristics, and subsequent treatment of the infused inorganic or organic material as well as other aspects relating to the interaction between infused materials and the polymer into which it is infused can be found hereinabove.

The oxyhalopolymer composites of the present invention can be prepared, for example, by the methods which follow, to which the present invention also relates.

One method for making an oxyhalopolymer composite according to the present invention includes providing an oxyhalopolymer which has free volume therein and in which at least a portion of the oxyhalopolymer's surface halogen atoms are substituted with hydrogen atoms and oxygen atoms or oxygen-containing radicals. The oxyhalopolymer's free volume is evacuated, and inorganic or organic molecules are infused into the evacuated free volume of the oxyhalopolymer.

The oxyhalopolymer can be prepared by providing a halopolymer and modifying the halopolymer's surface halogen atoms under conditions effective to substitute at least a portion, typically from about 1 to about 98%, preferably from about 3 to about 70% of the halopolymer's surface halogen atoms with hydrogen atoms and oxygen atoms or oxygen-containing radicals. In a preferred embodiment, the halopolymer's surface halogen atoms are modified by radio frequency glow discharge of a gas-vapor under vacuum by contacting the halopolymer with a gas/vapor plasma mixture while exposing the halopolymer to at least one radio frequency glow discharge under vacuum and under conditions effective to substitute

at least a portion of the halopolymer's halogen atoms with covalently bonded hydrogen atoms and oxygen atoms or oxygen-containing radicals.

5 In another method for making an oxyhalopolymer composite according to the present invention, a halopolymer composite is provided. The halopolymer composite includes a halopolymer having free volume therein and an inorganic or organic material disposed in the free volume of the halopolymer. The halopolymer composite's surface halogen atoms are then modified under conditions effective to substitute at least a portion of the halopolymer composite's surface halogen atoms with hydrogen atoms and oxygen atoms or oxygen-containing radicals. In a preferred embodiment, the halopolymer composite's surface halogen atoms are modified by a radio frequency glow discharge of a gas-vapor under vacuum by contacting the halopolymer composite with a gas/vapor plasma mixture while exposing the halopolymer composite to at least one radio frequency glow discharge under vacuum and under conditions effective to substitute at least a portion of the halopolymer composite's halogen atoms with covalently bonded hydrogen atoms and oxygen atoms or oxygen-containing radicals.

10 The halopolymer composite used in this method can be prepared by providing a halopolymer having free volume therein, evacuating the free volume of the halopolymer, and infusing inorganic or organic molecules into the evacuated free volume of the halopolymer.

20 The present invention also relates to methods for making a surface-oxyhalogenated non-halopolymer composites.

One such method includes providing a surface-oxyhalogenated non-halopolymer having natural free volume therein. The surface of the surface-oxyhalogenated non-halopolymer is oxyhalogenated. That is, the surface is modified with molecularly bonded halogen atoms or a halocarbon or halohydrocarbon film, and at least a portion of the molecularly bonded halogen atoms or the halocarbon or halohydrocarbon film's surface halogen atoms are substituted with hydrogen atoms and oxygen atoms or oxygen-containing radicals. The method further includes evacuating the free volume of the surface-oxyhalogenated non-halopolymer, and infusing inorganic or organic molecules into the evacuated free volume of the surface-oxyhalogenated non-halopolymer.

The surface-oxyhalogenated non-halopolymer can be prepared by providing a surface-halogenated non-halopolymer which has natural free volume therein and which has a surface that is modified with molecularly bonded halogen atoms or a halocarbon or halohydrocarbon film. In a preferred embodiment, the surface-halogenated non-halopolymer's surface halogen atoms are modified by contacting the surface-halogenated non-halopolymer with a gas/vapor plasma mixture while exposing the surface-halogenated non-halopolymer to at least one radio frequency glow discharge under vacuum and under conditions effective to substitute at least a portion of the surface-halogenated non-halopolymer's surface halogen atoms with covalently bonded hydrogen atoms and oxygen atoms or oxygen-containing radicals.

Surface-halogenated non-halopolymers suitable for use in this method can be made by providing a non-halopolymer (which has free volume therein) and contacting the non-halopolymer's surface with halogen atoms or a halocarbon or halohydrocarbon material under conditions effective to molecularly bond halogen atoms or a halocarbon or halohydrocarbon film to the non-halopolymer's surface.

In cases where the surface-oxyhalogenated non-halopolymer includes a non-halopolymer having a surface that is modified with a halocarbon or halohydrocarbon film (as opposed, for instance, to molecularly bonded halogen atoms) and where both the non-halopolymer and the halocarbon or halohydrocarbon film have free volumes therein, the method can, optionally, further include evacuating the free volume of the halocarbon or halohydrocarbon film and infusing inorganic or organic molecules into the evacuated free volume of the halocarbon or halohydrocarbon film. In this manner, both the non-halopolymer and the halocarbon or halohydrocarbon film disposed thereon can be infused with the inorganic or organic molecules.

In another method for making a surface-oxyhalogenated non-halopolymer composite according to the present invention, a surface-halogenated non-halopolymer composite is provided. The surface-halogenated non-halopolymer composite includes a non-halopolymer having free volume therein and an inorganic or organic material disposed in the free volume of the non-halopolymer. The surface-halogenated non-halopolymer composite also has a surface that is modified with molecularly bonded halogen atoms or with a molecularly bonded halocarbon or halohydrocarbon film. The method further includes modifying the surface-halogenated non-halopolymer composite's surface halogen atoms under conditions effective to substitute at least a

portion of the surface-halogenated non-halopolymer composite's surface halogen atoms with hydrogen atoms and oxygen atoms or oxygen-containing radicals. In a preferred embodiment, the surface-halogenated non-halopolymer composite's surface halogen atoms are modified by contacting the surface-halogenated non-halopolymer composite with a gas/vapor plasma mixture while exposing the surface-halogenated non-halopolymer composite to at least one radio frequency glow discharge under vacuum under conditions effective to substitute at least a portion of the surface-halogenated non-halopolymer composite's surface halogen atoms with covalently bonded hydrogen atoms and oxygen atoms or oxygen-containing radicals.

Surface-halogenated non-halopolymer composites suitable for use in the practice of this method of the present invention can be prepared, for example, by providing a surface-halogenated non-halopolymer having free volume therein and having a surface that is modified with molecularly bonded halogen atoms or a halocarbon or halohydrocarbon film. The surface-halogenated non-halopolymer's free volume is then evacuated, and inorganic or organic molecules are infused into the evacuated free volume of the surface-halogenated non-halopolymer.

In cases where the surface-halogenated non-halopolymer comprises a non-halopolymer having a surface that is modified with a halocarbon or halohydrocarbon film (as opposed to molecularly bonded halogen atoms) and where both of the non-halopolymer and the halocarbon or halohydrocarbon film have free volumes therein, the method can further include evacuating the halocarbon or halohydrocarbon film's free volume and infusing inorganic or organic molecules thereinto.

Alternatively, surface-halogenated non-halopolymer composites can be prepared by providing a non-halopolymer composite, which includes a non-halopolymer having natural free volume therein and an inorganic or organic material disposed in the natural free volume of the non-halopolymer. The non-halopolymer composite's surface is then contacted with halogen atoms or a halocarbon or halohydrocarbon film under conditions effective to molecularly bond the halogen atoms or a halocarbon or halohydrocarbon film to the non-halopolymer composite's surface. In this method, the non-halopolymer composite can be prepared by providing a non-halopolymer having natural free volume therein, evacuating the free volume of the non-halopolymer, and infusing inorganic or organic molecules into the evacuated free volume of the non-halopolymer.

Methods for evacuating the free volumes, infusing inorganic or organic molecules into the evacuated free volumes, and modifying inorganic or organic molecules infused into the free volume of the oxyhalopolymer, the halopolymer, the surface-halogenated non-halopolymer, the non-halopolymer, or the halocarbon or halohydrocarbon film (generically referred to herein as "polymer") are described above.

The oxyhalopolymers and oxyhalopolymer composites and the surface-oxyhalogenated non-halopolymers and surface-oxyhalogenated non-halopolymer composites can be prepared, respectively, from halopolymers and halopolymer composites and from surface-halogenated non-halopolymers and surface-halogenated non-halopolymer composites by a variety of techniques.

A variety of methods for incorporating reactive oxygen functionality onto halopolymers are available and useful for this invention. These methods include plasma and corona discharge treatments, ion beam and electron beam bombardment, x-ray and gamma ray treatments, as well as a variety of wet chemical processes including treatments with sodium in liquid ammonia or sodium naphthalene in glycol ether or surface reduction with benzoin dianion. All of the above methods are described in detail in Lee et al., "Wet-process Surface Modification of Dielectric Polymers: Adhesion Enhancement and Metallization," IBM J. Res. Develop., 38(4) (July 1994), Vargo et al., "Adhesive Electroless Metallization of Fluoropolymeric Substrates" Science, 262:1711-1712 (1993), "Rye et al., "Synchrotron Radiation Studies of Poly(tetrafluoroethylene) Photochemistry," Langmuir, 6:142-146 (1990), and Tan et al., "Investigation of Surface Chemistry of Teflon. 1. Effect of Low Energy Argon Ion Irradiation on Surface Structure," Langmuir, 9:740-748 (1993), which are hereby incorporated by reference.

For example, one suitable method for introducing oxygen functionality involves exposing the surface halogen atoms of the halopolymer or halopolymer composite or the surface-halogenated non-halopolymer or surface-halogenated non-halopolymer composite to actinic radiation, e.g., ultraviolet, X-ray, or electron beam radiation, in the presence of oxygen-containing organic compounds commonly referred to as "organic modifiers". Examples of suitable organic modifiers include sodium 4-aminothiophenoxide ("SATP"), sodium benzhydroxide ("SBH"), disodium 2-mercapto-3-butoxide ("DDSMB"), and other strong reducing agents which facilitate

hydrogen or halogen abstraction in the presence of actinic radiation. In practice, the halopolymer or halopolymer composite or the surface-halogenated non-halopolymer or surface-halogenated non-halopolymer composite is immersed into one or more of the organic modifiers and simultaneously exposed to actinic radiation, such as UV radiation, for a prescribed length of time. Further details with regard to this method of introducing oxygen functionality is described in, for example, U.S. Patent No. 5,051,312 to Allmer, which is hereby incorporated by reference.

Preferably, the oxyhalopolymer or oxyhalopolymer composite or the surface-oxyhalogenated non-halopolymer or surface-oxyhalogenated non-halopolymer composite is prepared by introducing oxygen functionality onto the surface of the corresponding halopolymer or halopolymer composite or surface-halogenated non-halopolymer or surface-halogenated non-halopolymer composite by RFGD of a gas-vapor under vacuum.

Briefly, the halopolymer or halopolymer composite or surface-halogenated non-halopolymer or surface-halogenated non-halopolymer composite in an atmosphere of a gas/vapor mixture is exposed to a single or series of radio frequency glow discharges ("RFGD") at power loadings of less than or equal to 100 watts and pressures of under 1 Torr, more preferably, from about 50 to 200 mTorr.

Although not wishing to be held to any precise mode of action, the primary mechanism of the plasma treating process of the instant invention is believed to involve the transfer of energy to the gaseous ions directly to form charged ionized gas species, i.e., ion sputtering of the polymer at the gas-solid interface. The radio frequency glow discharge plasma gas ions become excited through direct energy transfer by bombarding the gas ions with electrons. Thus, by exposing the halopolymer or halopolymer composite or surface-halogenated non-halopolymer or surface-halogenated non-halopolymer composite to either a single or a series of radio frequency glow discharge gas/vapor plasmas, from about 1% to about 98% of the surface halogen atoms are permanently removed in a controlled and/or regulated manner and replaced with hydrogen atoms along with oxygen atoms or low molecular weight oxygen-containing radicals. Suitable gas vapor plasmas include those containing admixtures of hydrogen gas, preferably ranging from about 20% to about 99%, by volume, and about 1% to about 80%, by volume, of a liquid vapor, such as liquid vapor of water, methanol, formaldehyde, or mixtures thereof. Although

hydrogen is required in all instances, by itself, hydrogen is insufficient to introduce both hydrogen and oxygen moieties into the carbon polymer backbone. A nonpolymerizable vapor/H₂ mixture is necessary to introduce the required hydrogen and oxygen or functionalized moieties into the halopolymer without disrupting surface morphology. Use of pure gas mixtures, specifically H₂/O₂, gave inferior results. Representative radio frequency glow discharge plasmas and operating conditions are provided in Table 1 below.

TABLE 1

Starting Material	RPGD Mix Composition	Pressure (mTorr)	Time (Min.)	Depth (Å)	CALCULATED ATOMIC RATIOS (ESCA)			
					C/O	C/F	F/O	Stoichiometry
Unmodified PTFE	--	--	--	--	0c	0.45	0c	C ₂ F ₂
Unmodified PVDF	--	--	--	--	0c	1.0	0c	C ₂ F ₂
Modified PTFE	2% H ₂ O 98% H ₂	150	20	100	7.5	1.5	5.0	C _{1.5} F _{1.5} H _{1.5} O _{1.5}
Modified PTFE	2% H ₂ O 98% H ₂	200	10	100	8.6	0.91	9.7	C _{1.5} F _{1.5} H _{1.5} O _{1.5}
Modified PTFE	20% MeOH(g) 80% H ₂	150	30	100	3.0	1.5	2.0	C ₂ F ₂ H ₂ O ₂
Modified PTFE	20% MeOH(g) 80% H ₂	200	5	100	9.3	2.0	4.7	C _{1.5} F _{1.5} H _{1.5} O _{1.5}
Modified PVDF	2% H ₂ O 98% H ₂	200	10	100	8.0	16.0	0.48	C _{1.5} F _{1.5} H _{1.5} O _{1.5}

Through specific and controlled addition of oxygen functionality via radio frequency glow discharge, the oxyhalopolymer composites and surface-oxyhalogenated non-halopolymer composites disclosed herein may remain resistant to fouling and adsorption of substances, a property which is consistent with the unmodified halopolymer composites. However, unlike unmodified halopolymer composites, such as PTFE composites, it was found that the oxyhalopolymer composites have the unique ability to react cleanly and rapidly with various atoms, molecules, or macromolecules through the oxygen containing groups (e.g., hydroxyl, carboxylic acid, ester, aldehyde, and the like) on the oxyhalopolymer composite surface to form refunctionalized oxyhalopolymer composites. This is especially advantageous because generally halopolymer composites are inert to wet and physical-chemical surface processes, at least to those which do not also induce substantial surface morphological damage. In addition, due to the relative inertness

of oxyhalopolymer composite surfaces, the ability to incorporate reactive functionality onto their surfaces creates a material which is specifically and controllably reactive while also being inert to other chemical and environmental concerns, e.g., adsorption of surface contaminants.

5 Further details with regard to this method are described in, for example, U.S. Patent Nos. 4,946,903, 5,266,309, and 5,627,079, all to Gardella, Jr. et al. (collectively, "Gardella") and applicants' copending U.S. Patent Application Serial No. 08/689,707 ("the '707 Application"), which are hereby incorporated by reference.

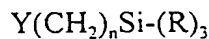
10 The surfaces of non-halopolymers and non-halopolymer composites can be halogenated by a variety of techniques. For example, halogenation can be carried out by adding fluorine or fluorocarbon coatings in the form of films. Non-halopolymers, such as the polyolefins, for example, can have their surfaces halogenated by either gasphase surface halogenation processes, or, alternatively, they
15 can be coated with a fluorocarbon based plasma film. Both processes are well known and documented in the prior art. Typically, with gas phase fluorination, non-halopolymers are exposed to a mixture of fluorine and nitrogen, whereby fluorine atoms become bonded to the polymer surface at the molecular level. Lagow et al., "Direct Fluorination: A 'New' Approach to Fluorine Chemistry," in Lippard, ed.,
20 Progress in Inorganic Chemistry, vol. 26, pp. 161ff (1979), which is hereby incorporated by reference, discloses methods of gas phase surface fluorination for providing antireflective, low surface energy films to various commercially available base polymers, such as highly cross-linked polyethylene, polypropylene, poly(methyl methacrylate), polycarbonate, polyester, polystyrene, and polymethylpentene. Clark
25 et al., "Applications of ESCA to Polymer Chemistry. 6. Surface Fluorination of Polyethylene -- Application of ESCA to Examination of Structure as a Function of Depth," J. Polym. Sci., Polymer Chem. Ed., 13:857-890 (1975), which is hereby incorporated by reference, also discloses the surface fluorination of high density polyethylene films. Other suitable gas phase fluorination methods are described in,
30 for example, U.S. Patent Nos. 3,988,491 and 4,020,223 to Dixon et al., which are hereby incorporated by reference.

Methods for preparing fluorocarbon plasma deposited films are also well documented in the literature. For instance, Haque et al., "Preparation and Properties

of Plasma-Deposited Films With Surface Energies Varying Over a Wide Range," J. App. Polym. Sci., 32:4369-4381 (1986), which is hereby incorporated by reference, discloses suitable methods for modification of polymer surfaces with plasma deposited thin films using a capacitatively coupled RF-discharge system.

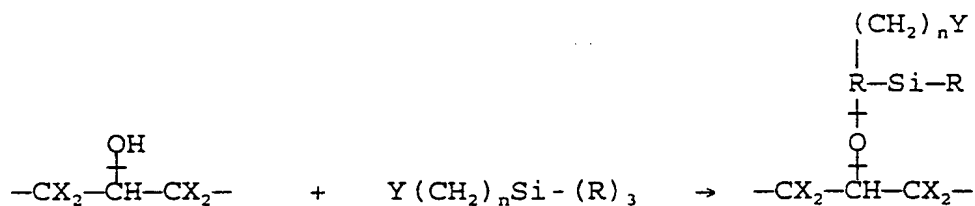
5 Representative useful fluorinated gaseous materials include hexafluoroethylene, perfluoropropane, and hexafluoropropene. Nakajima et al, "Plasma Polymerization of Tetrafluoroethylene," J. App. Polym. Sci., Vol. 23, 2627-2637 (1979), which is hereby incorporated by reference, discloses methods for applying plasma polymerized fluorocarbon coatings which can be utilized for generating surfaces
10 having, for example, low dielectric and non-corrosive properties. U.S. Patent No. 4,718,907 to Karwoski et al., which is hereby incorporated by reference, describes useful methods for introducing fluorinated coatings for vascular grafts and other biomedical technologies. Alternatively, thin (about 0.5 μm to about 50 μm) or thick (about 50 μm to several mm) halopolymer (e.g., PTFE, PVDF, PFA, MFA, ECTFE,
15 and PCTFE) films can be bonded to the non-halopolymers or non-halopolymer composites, for example, by methods which are well known in the art.

Optionally, the oxyfluoropolymer composite or the surface-oxyhalogenated non-halopolymer composite of the present invention can be refunctionalized. The types of functionalities with which the oxyfluoropolymer composite's or the surface-
20 oxyhalogenated non-halopolymer composite's surfaces can be refunctionalized include all those which can be reacted with hydroxyl, carboxylic acid, ester, and aldehyde groups bonded through the halopolymer backbone or surface halogen atom by means of reactions generally familiar among those skilled in the art. The reactivity of the surface of the oxyhalopolymer composite is determined by the
25 particular type of oxygen functionality. For instance, silanes of the silicon-containing organic or inorganic class react vigorously with hydroxyl groups forming a silanol linkage or coupled bond. However, the rate of reaction is enhanced even further due to the close proximity of the reactive oxygen functionality to the electronegative halogen atom(s). This is believed to provide for extremely rapid
30 reaction rates through stabilization of the oxygen anion. The preferred refunctionalized oxyhalopolymer composites or surface-oxyhalogenated non-halopolymer composites can be prepared with a wide range of organosilane coupling agents having the general Formula I:



wherein Y is selected from the group consisting of allyl, alkyl, haloalkyl, amino, mercapto, epoxy, glycidoxy, methacrylate, cyano, and $-CH_2CO_2$ -alkyl; n is from 0 to about 17; and R is independently selected from hydrogen, halogen, alkyl, haloalkyl, alkylamino, alkoxy, and trialkylsiloxy. The silane coupling agents are known materials which are commercially available, such as from Petrarch Systems, Bristol, Pennsylvania.

The process of preparing the organosilicon substituted oxyhalopolymer composites or surface-oxyhalogenated non-halopolymer composites can be illustrated by the following reaction:



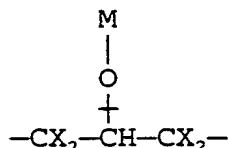
wherein X is halogen (e.g., F or Cl), and R, Y, and n are the same as in Formula I.

In the above reaction scheme, the first reactant represents the oxyhalopolymer composite surface or the surface-oxyhalogenated non-halopolymer composite surface, and the second reactant is the organosilane coupling agent set forth above having Formula I. Preferably, the refunctionalized oxyhalopolymer composites and surface-oxyhalogenated non-halopolymer composites are prepared using organosilane coupling agents in which Y is alkylamino, dialkylamino, mercapto, or glycidoxy and in which R is chlorine, bromine, fluorine, alkyl having from 1 to 4 carbon atoms, chloromethyl, monoethylamino, dimethylamino, methoxy, ethoxy, propoxy, butoxy, or trimethylsiloxy. Specific representative organosilanes are 3-aminopropyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, and 3-glycidoxypropyltrimethoxysilane to name but a few.

Other particularly useful functionalities which may be covalently bonded with the oxyfluoropolymer composites and surface-oxyhalogenated non-halopolymer composites of the present invention through their reactive oxygen-containing sites include fluorophores. As used herein, fluorophores include organic compounds that

may fluoresce. The preferred fluorophores are the isothiocyanate substituted types, such as fluorescein isothiocyanate ("FITC"), malachite green isothiocyanate, rhodamines (e.g., tetramethylrhodamine isothiocyanate ("TRITC")), and the like. Other suitable isothiocyanate substituted fluorophores are described in Haugland, Handbook of Fluorescent Probes and Research Chemicals, Molecular Probes, Inc. (1989), which is hereby incorporated by reference and are available from Molecular Probes, Inc. Oxyhalopolymer composites and surface-oxyhalogenated non-halopolymer composites that are refunctionalized with isothiocyanate substituted fluorophores are especially useful in a wide variety of probes and sensors, such as for nucleic acids.

In addition to the organosilicon and fluorophore refunctionalized oxyhalopolymer composites and surface-oxyhalogenated non-halopolymer composites, other representative examples include alkali metal derivatives of the oxyhalopolymer composites and surface-oxyhalogenated non-halopolymer composites, such as those having the formula:



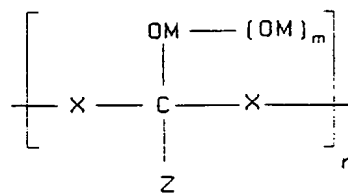
where M is an alkali metal (e.g., Li, Na, and K), and X is a halogen, particularly F. These oxyhalopolymer composites and surface-oxyhalogenated non-halopolymer composites can be prepared, for example, by reacting solutions of alkali metal hydroxide (e.g., LiOH, NaOH, KOH, and combinations thereof) with the oxygen containing groups of the oxyhalopolymer composites and surface-oxyhalogenated non-halopolymer composites. The alkali metal oxyhalopolymer composites and surface-oxyhalogenated non-halopolymer composites are useful as cell separators in electrochemical cells, such as energy producing cells (e.g., batteries).

Further details with respect to refunctionalization can be found in, for example, U.S. Patent No. 5,266,309 to Gardella, Jr. et al., which is hereby incorporated by reference. As used herein, the oxyhalopolymers, oxyfluoropolymer composites, surface-oxyhalogenated non-halopolymers, and surface-oxyhalogenated non-halopolymer composites of the present invention are meant to include those

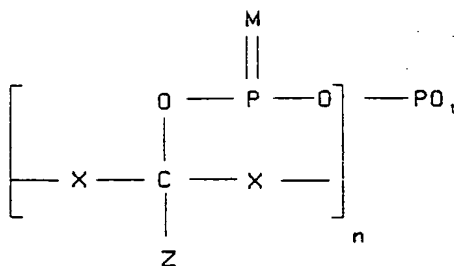
which contain oxygen or oxygen-containing radicals which have been refunctionalized as described above.

The oxyfluoropolymer composite or the surface-oxyhalogenated non-halopolymer composite of the present invention can, optionally, be metallized with one or more transition metals. The transition metals are bonded, preferably covalently, to the oxyfluoropolymer composite or the surface-oxyhalogenated non-halopolymer composite via the oxygen or oxygen-containing radicals which substitute for surface halogen atoms of the oxyfluoropolymer composite or the surface-oxyhalogenated non-halopolymer composite. When metallized as described herein, the oxygen or oxygen-containing radicals are preferably present not only at the immediate surface but also to a depth of from about 10 Å to about 200 Å. This will form a molecular layer of the transition metal bonded, preferably covalently, to the oxygen sites or a multi-molecular film of transition metal from about 10 Å to more than about a micron in thickness stabilized by an initial molecular layer of transition metal. The oxyfluoropolymer composites and the surface-oxyhalogenated non-halopolymer composites of the present invention are meant to include those which contain oxygen or oxygen-containing radicals that have been metallized as described above. The metallized oxyhalopolymer composites and surface-oxyhalogenated non-halopolymer composites of the present invention may, hereinafter, be referred to as metallohalopolymers ("MHPs").

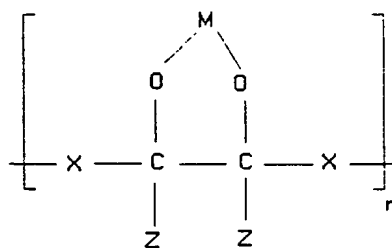
Representative MHPs include those which contain, at the surface thereof, one or more repeating non-terminal units having the formulae:



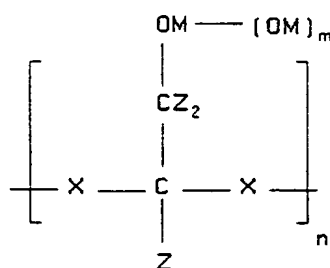
5



10

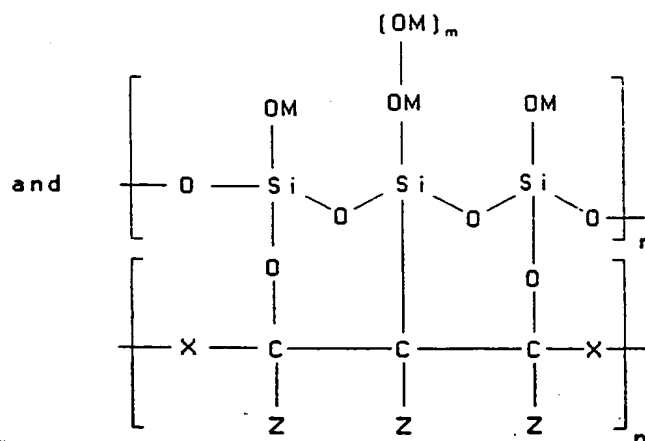


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25



30

wherein M is a transition metal; Z a halogen (e.g., fluorine, chlorine), hydrogen, -
(CH₂)_yCH₃, -CH₃ or -OR; R is hydrogen, -(CH₂)_yCH₃, or -CH₃; y is 1 to 20; X is a
5 methylene group optionally substituted with one or two halogen atoms (e.g., CF₂,
CFCI, CCl₂, CFH, CCIH, and CH₂); n is 10 to 1000; t is 2 to 3; and m is 0 to 1000.

The metals are capable of being covalently bonded in controlled amounts,
and with predetermined valences. The concentration of transition metal introduced
into the polymer may be controlled, for example, by kinetics where the reaction
10 speed depends on a variety of conditions including, (i) the solution chemistry
utilized; (ii) the binding strength of the ligand on the organometallic complex
starting material which is dissociated during the reaction to form the MHP, and
(iii) the use of gas phase as opposed to solution phase (e.g., solution phase could
react to form metalloxo functional groups at the oxyfluoropolymer surface whereas a
15 chemical vapor deposition could react to form both a metalloxo bond plus deposit
an additional overlayer of metal onto the metalloxo functionality).

Alternatively, metal concentration of the MHP may be controlled by the
amount of oxygen functionality initially present in the starting oxyfluoropolymer
material which can be controlled by methods described in Gardella and in U.S.
20 Patent No. 5,051,312 to Allmer, which are hereby incorporated by reference.

Methods for controlling the oxidation state of the metal of the MHP are also
varied. For instance, one can construct a Rh⁺³ MHP according to the invention by
depositing rhodium from an aqueous solution containing RhCl₃ wherein the oxidation
state of the rhodium in the starting organometallic complex is +3. Alternatively, a
25 Rh⁰ MHP can be made by depositing RhCl₃ from a solution containing ethanol. In
this case, the Rh⁺³ of the starting organometallic complex is reduced by the presence
of alcohol during the reaction to the oxyhalopolymer composite or surface-
oxyhalogenated non-halopolymer composite in order to form the Rh⁰ MHP. Thus, in
this case, control of the oxidation state may be achieved by adding an appropriate
30 reducing agent to the reaction solution which will effectively lower the oxidation
state of the starting metal contained in the organometallic starting material.

In general, the oxidation state of the metal contained in the organometallic
starting material can be preserved and, thus, further controlled by choosing an

organometallic starting material containing the transition metal in the desired oxidation state. Thus, for example, to make a MHP with Cu^{+2} , a CuCl_2 organometallic starting material could be reacted with an oxyhalopolymer composite or a surface-oxyhalogenated non-halopolymer composite by exposing the oxyfluoropolymer composite or a surface-oxyhalogenated non-halopolymer composite to a millimolar solution of CuCl_2 in a suitable solvent (e.g., dimethylformamide ("DMF")). A Cu^{+1} MHP could be prepared by exposing an oxyfluoropolymer to a millimolar solution of CuSCN in 0.5M NH_4OH . Cu^0 MHP may be prepared by adding an effective reducing agent to the reaction solutions or by immersing Cu^{+1} or Cu^{+2} MHP materials in a bath containing an appropriate reducing agent for copper, such as NaBH_4 .

A further alternative for controlling the oxidation state of the transition metal of the MHPs of this invention comprises utilizing the strength of the ligands making up a particular organometallic complex starting material. For example, $\text{Cr}(\text{CO})_6$ (chromium hexacarbonyl) represents Cr in a zero oxidation state. The carbonyl ligands are relatively weakly bound, so that all six of them can be liberated during the reaction with an oxyhalopolymer composite or a surface-oxyhalogenated non-halopolymer composite to yield a Cr^{+6} MHP. Alternatively, trisalkylphosphine chromium (III) chloride ($(\text{PR}_3)_3 \text{CrCl}_3$) has three labile chlorine ligands and three relatively stable trialkylphosphine ligands. Upon reacting with an oxyfluoropolymer, the chromium in trisalkylphosphine chromium (III) chloride loses the three chlorine ligands but retains the three trialkylphosphines. As a result a Cr^{+3} MHP is produced.

It will be understood that above-described refunctionalization or metallization processes can take place at any stage of the aforescribed process of the present invention for making the oxyhalopolymer composite or the surface-oxyhalogenated non-halopolymer composite once the oxygen functionality has been introduced onto the polymer composite's or polymer's halogen or halogenated surface. For example, metallization or refunctionalization can be carried out on the oxyhalopolymer composite or the surface-oxyhalogenated non-halopolymer composite. Alternatively, metallization or refunctionalization can be carried out subsequent to modifying surface halogens of the halopolymer or surface-halogenated non-halopolymer but prior to evacuating and infusing with the inorganic or organic

material. In some cases, depending on the nature of the infused inorganic or organic material, metallization (or refunctionalization) and infusing can be carried out in one step simply by contacting the evacuated oxyhalopolymer or surface-oxyhalogenated non-halopolymer with the inorganic or organic material under conditions that are effective to both infuse the inorganic or organic material into the evacuated free volume and react with the surface oxygen or oxygen-containing radicals.

Further details with regard to metallization of halogenated surfaces containing covalently bonded oxygen or oxygen-containing radicals can be found in, for example, applicants' copending '707 Application, which is hereby incorporated by reference. Applicants' copending '707 Application, which is hereby incorporated by reference, also describes the uses to which the metallized oxyhalopolymer composite or the metallized surface-oxyhalogenated non-halopolymer composite of the present invention can be put.

Metallization and refunctionalization of the oxyhalopolymer composite or the surface-oxyhalogenated non-halopolymer composite can be either over the entire exposed surface or on selected regions. For example, the regions selected for metallization or refunctionalization can be in the form of a predetermined pattern. Metallization and refunctionalization in predetermined patterns can be effected by using oxyhalopolymers, oxyhalopolymer composites, surface-oxyhalogenated non-halopolymers, or surface-oxyhalogenated non-halopolymer composites whose surface halogen atoms are substituted with oxygen or oxygen-containing radicals in the desired predetermined pattern. These patterned oxyhalopolymers, oxyhalopolymer composites, surface-oxyhalogenated non-halopolymers, or surface-oxyhalogenated non-halopolymer composites can be produced by masking the halopolymer, halopolymer composite, surface-halogenated non-halopolymer, or surface-halogenated non-halopolymer composite and introducing oxygen functionalities into the halogen or halogenated surface thereof, such as by RFGD of a gas vapor. After exposure of the masked halopolymer composite or halopolymer or the masked surface-halogenated non-halopolymer composite or surface-halogenated non-halopolymer, only the unmasked portions have oxygen or oxygen-containing radicals at the surface. When the patterned oxyhalopolymer composites or oxyhalopolymers or the patterned surface-oxyhalogenated non-halopolymer composites or surface-oxyhalogenated non-halopolymers are exposed to metallizing or refunctionalizing

conditions, as described above, metallization or refunctionalization takes place only in those regions which have oxygen or oxygen-containing radicals at the surface.

In cases where a non-halopolymer is used, the metallized or refunctionalized pattern can also be controlled by using a non-halopolymer which is modified, in the predetermined pattern, with molecularly bonded halogen atoms or a halocarbon or halohydrocarbon film. When oxygen functionality is introduced into such a surface-halogenated non-halopolymer, only those portions of the non-halopolymer surface that have been surface-halogenated will have oxygen or oxygen-containing radical, and, therefore, upon metallization or refunctionalization, a patterned metallized or refunctionalized surface-oxyhalogenated non-halopolymer composite or a patterned metallized or refunctionalized surface-oxyhalogenated non-halopolymer is produced. As is implicit in the above discussion, modification of the non-halopolymer substrate's surface with molecularly bonded halogen atoms or a halocarbon or halohydrocarbon film in the predetermined pattern can take place before or after evacuation and infusion of the organic or inorganic materials.

Methods pertaining to patterning include conventional photoresist based photolithography, in which the modified halogenated surface is coated with a photoresist material, exposed to radiation, and developed to expose a pattern. The exposed patterns are then reacted with a preferred material (e.g., organometallic species), vapor deposited metals (including oxides, nitrides, etc., thereof), organic molecules, biological molecules, or polymers), and the unexposed photoresist material is removed through conventional methods to produce a patterned surface. Further details regarding this method can be found in, for example, Moreau, Semiconductor Lithography - Principles, Practices, and Materials, New York:Plenum Press (1988) (particularly Chapters 8 & 9 (pp. 365-458)), which is hereby incorporated by reference.

Additionally, the halogenated surface can be reacted with photolabile chemical functionality which, upon using conventional masking techniques and exposure to actinic radiation, produces selective sites which are capable of bonding organometallic species, vapor deposited metals (including oxides, nitrides, silicides, and borides, etc., thereof), organic molecules, biological molecules, or polymer species only to the exposed regions which become active towards refunctionalization. Details with respect to this method can be found in, for example, U.S. Patent Nos.

5,077,085 and 5,079,600 to Schnur et al., which are hereby incorporated by reference.

The composites of the present invention contain polymeric phases which have physical properties substantially similar to the properties of the native polymer (i.e., polymer in the absence of inorganic or organic molecules or macromolecular networks). Consequently, the composites of the present invention, relative to conventional inorganic-organic hybrid materials, have significantly more predictable mechanical properties. The composites of the present invention also have controllable, predictable, and reproducible levels of optical densities and electrical, ionic, and charged species conductivities, which make them useful in various applications including photoradiation shields and filters, electromagnetic radiation shields and filters, and conducting electrodes. These characteristics also make these composites useful as components in the construction of electrolytic cells, fuel cells, optoelectronic devices, semiconductors for microelectronic applications, materials having flame and heat retardant properties, coatings which inhibit fouling by organisms, and heterogeneous catalytic substrates. When the composite of the present invention is used as a catalyst, it is sometimes desirable to swell the composite during or before its use as a catalyst to increase the rate of diffusion of reactant into the composite. This can be carried out by exposing the composite to standard supercritical conditions. For example, the composite can be placed in a vessel capable of withstanding high pressures, such as the pressures commonly encountered in supercritical catalytic processes. The vessel is then charged with a supercritical fluid under supercritical conditions, such as carbon dioxide at 2500 psi, and the pressure is maintained for a period of time ranging from 1 to 100 hours. As a result of being exposed to these supercritical conditions, the composite swells. However, in contrast to the materials of the prior art in which impregnation is carried out under supercritical conditions, the inorganic or organic materials infused in accordance with the methods of the present invention do not diffuse out of the polymer upon the composite's subsequent exposure to supercritical conditions. Details with respect to these uses are set forth in applicants' copending U.S. Patent Application Serial No. 08/833,290; U.S. Patent Application Serial No. 08/955,901; U.S. Patent Application Serial No. 08/997,102; and U.S. Provisional Patent Application Serial No. 60/039,258, which are hereby incorporated by reference.

In addition, the composites of the present invention have a surface containing halogen atoms, a portion of which have been replaced with hydrogen atoms and oxygen atoms or oxygen-containing groups. The oxyhalopolymer or surface-oxyhalogenated non-halopolymer surface retains many of the positive attributes characteristic of halogenated surfaces, such as tendency to repel water and other polar solvents, high thermal stability, low adhesion and friction coefficients. However, unlike halogenated surfaces, the surfaces of the oxyhalopolymer composites and surface-oxyhalogenated non-halopolymer composites of the present invention have reactive chemical sites which are either bonded to or permit bonding with other chemical functionalities, such as organosilicons, organometallic precursors, transition metal ions and compounds, transition metal films, fluorescent compounds, dyes, biological materials, such as proteins, enzymes, and nucleic acids.

The composites of the present invention are particularly useful for producing conducting and semiconducting films (e.g., metals, metal oxides, metal nitrides, metal carbides, metal borides, polyacetylenes, polythiophenes, and polypyrroles) on the surfaces of halopolymers. More particularly, the conducting and semiconducting films are easier to dispose on the surfaces of the composites of the present invention than on the surfaces of halopolymer composites. Referring to Figure 1, it has been observed that, when halopolymer 20 having free volume therein is evacuated and inorganic or organic materials are infused into halopolymer 20's evacuated free volume to produce halopolymer composite 22, the infused organic or inorganic materials reside in the bulk of halopolymer composite 22. It has also been observed that there exists thin layer 24 (typically from about 0.5 nm to about 3 nm thick) of halopolymer adjacent halopolymer composite 22's surface 26 that contains no infused inorganic or organic material. In many applications, it is important that the inorganic or organic layer be present directly at surface 26 of halopolymer composite 22 to provide a more compatible bonding environment to an adjacent conducting or semiconducting material (e.g., metal, metal oxide, metal nitride, metal carbide, metal boride, polyacetylene, polythiophene, and polypyrrole). In particular, semiconductor materials, such as metal oxides, metal nitrides, metal carbides, or metal borides, are currently synthesized, mixed, or coated with fluorine or fluoropolymers (e.g., PTFE or PVDF), because of the fluoropolymers' physical and chemical inertness and dielectric properties. See, for example, Kirschner, Chemical

and Engineering News, 75(47):25 (November 24, 1997), U.S. Patent No. 5,602,491 to Vasquez et al., U.S. Patent No. 5,491,377 to Janusauskas, U.S. Patent No. 5,287,619 to Smith et al., U.S. Patent No. 5,440,805 to Daigle et al., and U.S. Patent No. 5,061,548 to Arthur et al., which are hereby incorporated by reference.

5 However, it is also desirable to adhere layers or films of inorganic or organic materials (e.g., conducting, semiconducting, or luminescent materials) adjacent to the fluoropolymeric materials to provide a conducting or semiconducting layer on the semiconductor which has been synthesized, mixed, or coated with fluorine, or fluoropolymers. Similarly, where a halopolymer composite is substituted for the
10 semiconductor materials which has been synthesized, mixed, or coated with fluorine or fluoropolymers, it may be desirable to adhere layers or films of inorganic or organic materials (e.g., conducting, semiconducting, or luminescent materials) adjacent to the halopolymer composite. For example, in some cases, it is desirable to bond the halopolymer composite in between conducting or semiconducting
15 materials. However, referring again to Figure 1, since it has been observed that the infused conducting or semiconducting material contained within halopolymer composite 22 lies from about 0.5 nm to about 3 nm below surface 26 of halopolymer composite 22, the infused material does not facilitate adhesion of the desired conducting or semiconducting material to surface 26 of halopolymer
20 composite 22.

The composites of the present invention (i.e., the oxyhalopolymer composites or surface-oxyhalogenanted non-halopolymer composites of the present invention) and composites made in accordance with the methods of the present invention are completely infused in the bulk and, in some cases, contain a layer
25 (from about 1nm to about 1mm thick) of pure conducting or semiconducting material (e.g., metal, metal oxide, metal nitride, metal carbide, metal boride, polyacetylenes, polythiophene, and polypyrrole) on the surface of the infused matrix. This is illustrated in Figure 2. Oxyhalopolymer composite 30 includes halopolymer composite 32 on whose surface 34 is covalently bonded oxygen atoms or oxygen-
30 containing groups 36, which, in Figure 2, are designated X. The thin layer 38 (typically from about 0.5 nm to about 3 nm thick) adjacent surface 34 is also infused with inorganic or organic material, and, in some cases, layer 40 (from about 1nm to about 1mm thick) of pure conducting or semiconducting material is disposed on

surface 34 of oxyhalopolymer composite 30. Thus, using the methods of the present invention, a composite having organic or inorganic material infused into the entire volume of the polymer matrix can be prepared. More particularly, the organic or inorganic material can extend from the surface of the polymer matrix and,
5 optionally, from 1 nm to several mm above the surface of the polymer matrix.

The composites of the present invention serve particularly well as substrates for bonding conducting or semiconducting materials (e.g., metals, metal oxides, metal nitrides, metal carbides, metal borides, polyacetylenes, polythiophenes, and polypyrroles), other polymers (e.g., polyurethanes, polyimides, polyamides,
10 polyphosphazenes, halopolymers, polyolefins, polyacrylates, and polyesters), biological materials (e.g., proteins, enzymes, nucleotides, antibodies, and antigens), and phosphorescent and fluorescent molecules commonly used in sensors and electroluminescent or liquid crystal based displays. This is illustrated in Figures 3 and 4.

For example, in Figure 3, halopolymer 42 is surface treated so that oxygen atoms or oxygen-containing radicals (designated X) 43 are bonded to surface 44, thus producing oxyhalopolymer 45. Oxyhalopolymer 45 is then infused with an organic or inorganic material to produce oxyhalopolymer composite 46. During the infusion process, layer 47 (from about 1nm to about 1mm thick) of pure conducting
20 or semiconducting material (e.g., metal, metal oxide, metal nitride, metal carbide, metal boride, polyacetylenes, polythiophene, and polypyrrole) is disposed on surface 44. Layer 47 of oxyhalopolymer composite 46 is then reacted with material (designated Y) 48 (e.g., conducting or semiconducting materials, other polymers, biological materials, and phosphorescent and fluorescent molecules commonly used
25 in sensors and electroluminescent or liquid crystal based displays) so that material (designated Y) 48 is bonded to layer 47 of oxyhalopolymer composite 46.

Alternatively, in some cases, it may be desirable to bond materials directly to the oxyhalopolymer composite or surface-oxyhalogenated non-halopolymer composite of the present invention without having a thick layer of pure conducting
30 or semiconducting material (e.g., metal, metal oxide, metal nitride, metal carbide, metal boride, polyacetylenes, polythiophene, and polypyrrole) on the surface of the composite. This can be facilitated, for example, by using the scheme depicted in Figure 4. In Figure 4, halopolymer 50 is infused with an organic or inorganic

material to produce halopolymer composite 52. Halopolymer composite 52 is then surface treated so that oxygen atoms or oxygen-containing radicals (designated X) 56 are bonded to surface 54 of halopolymer composite 52, thus producing oxyhalopolymer composite 58. Oxyhalopolymer composite 58's surface oxygen atoms or oxygen-containing radicals (designated X) 56 are then reacted with material (designated Y) 60 (e.g., conducting or semiconducting materials, other polymers, biological materials, and phosphorescent and fluorescent molecules commonly used in sensors and electroluminescent or liquid crystal based displays) so that material (designated Y) 60 is bonded to oxyhalopolymer composite 58. By using the scheme depicted in Figure 4, the thick bonding layer made of pure conducting or semiconducting material can be excluded from the resulting composite.

The oxyhalopolymer composites or surface-oxyhalogenated non-halopolymer composites of the present invention can be used to make electrical substrate materials well suited for forming rigid printed wiring board substrate materials and integrated circuit chip carriers, such as those described in U.S. Patent No. 4,849,284 to Arthur et al. ("Arthur"), which is hereby incorporated by reference, by, for example, substituting the oxyhalopolymer composites or surface-oxyhalogenated non-halopolymer composites of the present invention for the ceramic filled fluoropolymer set forth in Arthur.

The oxyhalopolymer composites or surface-oxyhalogenated non-halopolymer composites of the present invention can be used to make materials which exhibit low loss, and high dielectric constants and which have acceptable thermal coefficients of dielectric constants, such as those described in U.S. Patent No. 5,358,775 to Horn, III ("Horn"), which is hereby incorporated by reference, by, for example, substituting the oxyhalopolymer composites or surface-oxyhalogenated non-halopolymer composites of the present invention for the ceramic filled fluoropolymers set forth in Horn.

The oxyhalopolymer composites or surface-oxyhalogenated non-halopolymer composites of the present invention can be used to make solid polymer type fuel cells, such as those described in U.S. Patent No. 5,474,857 to Uchida et al. ("Uchida"), which is hereby incorporated by reference, by, for example, substituting the oxyhalopolymer composites or surface-oxyhalogenated non-halopolymer

composites of the present invention for the solid polymer electrolyte set forth in Uchida.

The oxyhalopolymer composites or surface-oxyhalogenated non-halopolymer composites of the present invention can be used to make coverlay films suitable for use in the making printed circuit boards, such as those described in U.S. Patent No. 5,473,118 to Fukutake et al. ("Fukutake"), which is hereby incorporated by reference, by, for example, substituting the oxyhalopolymer composites or surface-oxyhalogenated non-halopolymer composites of the present invention for the fluoropolymer film (which is subsequently coated with a thermoplastic or heat-curing adhesive) set forth in Fukutake.

The oxyhalopolymer composites or surface-oxyhalogenated non-halopolymer composites of the present invention can be used in manufacturing multilayer circuit assemblies, such as by the methods described in U.S. Patent No. 5,440,805 to Daigle et al. ("Daigle"), which is hereby incorporated by reference, by, for example, substituting the oxyhalopolymer composites or surface-oxyhalogenated non-halopolymer composites of the present invention for the fluoropolymer composite materials set forth in Daigle.

The oxyhalopolymer composites or surface-oxyhalogenated non-halopolymer composites of the present invention can be used in making multichip module substrates, such as those described in U.S. Patent No. 5,287,619 to Smith et al. ("Smith"), which is hereby incorporated by reference, by, for example, substituting the oxyhalopolymer composites or surface-oxyhalogenated non-halopolymer composites of the present invention for the fluoropolymer composite materials set forth in Smith.

The oxyhalopolymer composites or surface-oxyhalogenated non-halopolymer composites of the present invention can be used in making electroluminescent lamps, such as those described in U.S. Patent 5,491,377 to Janusauskas ("Janusauskas"), which is hereby incorporated by reference, by, for example, substituting the oxyhalopolymer composites or surface-oxyhalogenated non-halopolymer composites of the present invention for the fluoropolymer binder set forth in Janusauskas.

The composites of the present invention can be in freestanding form (i.e., not attached to another material). Examples of composites in freestanding form include composite beads, composite particles, composite films, composite fibers,

composite filaments, composite powders, and the like. Alternatively, the composites of the present invention can be disposed on a base material (e.g., a halopolymer, a non-halopolymer, a ceramic, a glass, a metal, and a metal oxide). For example, pure metal oxide substrates that are coated with composites (particularly oxyfluoropolymer composites) of the present invention (particularly those having a metal oxide surface and metal oxides disposed in the free volumes thereof that are coated onto pure metal oxide) are particularly useful in the semiconductor industry.

Oxyhalopolymer composites of the present invention disposed on a base material can be prepared, for example, by coating, adhering, or otherwise disposing a halopolymer on the base material and then modifying the surface with oxygen or oxygen-containing radicals and, prior to, during, or subsequent to said modifying, evacuating the free volume and infusing an inorganic or organic material thereinto. Alternatively, oxyhalopolymer composites of the present invention disposed on a base material can be prepared by coating, adhering, or otherwise disposing a halopolymer composite on the base material and then modifying the halopolymer composite's surface with oxygen or oxygen-containing radicals. Still alternatively, oxyhalopolymer composites of the present invention disposed on a base material can be prepared by coating, adhering, or otherwise disposing an oxyhalopolymer on the base material and then evacuating the oxyhalopolymer's free volume and infusing an inorganic or organic material thereinto. Still alternatively, oxyhalopolymer composites of the present invention disposed on a base material can be prepared by coating, adhering, or otherwise disposing an oxyhalopolymer composite on the base material.

Surface-oxyhalogenated non-halopolymer composites of the present invention disposed on a base material can be similarly prepared, for example, by any of the methods described above for preparing oxyhalopolymers disposed on base materials.

The present invention is further illustrated by the following examples.

EXAMPLES

Example 1 -- Preparation and Characterization of V_2O_5 in Polytetrafluoroethylene-co-hexafluoropropylene

5 A 12" x 2" piece of polytetrafluoroethylene-co-hexafluoropropylene, ("FEP") (Dupont), was wrapped around itself to form a loose fitting coil and then placed in a 100 ml round bottom flask. The flask was connected to a vacuum line and then pumped down to less than 10 mTorr pressure. Next, ca. 1 ml of $V(O)Cl_3$ (Ström) was vacuum transferred to the 100 ml round bottom flask. The flask was
10 then closed and heated to ca. 75°C under vacuum so that a gas phase of $V(O)Cl_3$ filled the entire volume of the flask for 1 hr. The flask was removed from the heat, and its temperature lowered to about room temperature. The $V(O)Cl_3$ was then vacuum transferred off the FEP polymer, and the 100 ml round bottom flask was opened to ambient air.

15 Upon opening the flask, the FEP polymer was transparent to the eye but, within a few minutes, began to turn yellow-orange and reached its darkest level after a few hours. X-Ray Photoelectron Spectroscopy ("XPS") indicated the formation of a highly oxidized vanadium complex, and the visible orange color was indicative of a large macromolecular V_2O_5 network. This was further confirmed by ultraviolet-
20 visible spectroscopy ("UV-vis"). The broad absorbance spectrum had two major peaks around 370 nm ($A = 1.8$) and 248 nm ($A = 3.2$) and was similar to but different than that of pure V_2O_5 powder dissolved in acetonitrile. It is believed that the difference in the UV-vis spectra between the V_2O_5 formed in the FEP polymer and that in the acetonitrile solution is attributable to some electronic coordination of
25 the vanadium metal center to adjacent fluorine functionality contained in the FEP. This is supported by the XPS results which measure an extremely high binding energy of about 518.5 eV, a full eV higher than that measured for the V_2O_5 powder. This increase in binding energy is consistent with the vanadium being in a highly electron withdrawing environment which further suggests that the vanadium is either
30 directly bonded to or affected through space by the fluorine functionality contained in the FEP polymer. To further support this, the FEP polymer containing the vanadium was placed into a beaker containing 50% hydrofluoric acid ("HF") in water for 2 hrs. Upon removing the FEP material, it was observed that the material

was totally transparent to the eye (i.e., no yellow color was observed). Inspection by UV-vis spectroscopy showed the absorbance band originally at 248 nm to be present (although it was blue shifted to a lower wavenumber) at approximately the same intensity. However, the band at 370 nm had disappeared. Since the band at 370 nm is attributed to intermolecular transitions and the band at 248nm is attributed to intramolecular transitions, the results are consistent with a mechanism which preferentially coordinates the vanadium species to fluoride ions from the HF. This in turn breaks the coordination of the vanadium to the fluorine atoms in the FEP polymer which then leads to a breakdown of the macromolecular network. This is also consistent with the loss of visible color (i.e., individual or low molecular weight macromolecules of V_2O_5 are transparent in the visible while large macromolecular networks show colors ranging from light yellow to orange). Upon removing this material from the HF solution, it was observed that the yellow color returned within a few hours and that the UV-vis spectrum obtained from this material showed the same features observed with the FEP material before it was exposed to the HF. This indicates not only that the macromolecular network was reformed and that the process is reversible, but also that other molecules can readily diffuse into and out of these materials and easily interact with the inorganic portion of the composite material.

The method described above can also be used to infuse vanadium oxide into other fluoropolymer resins, for example, PVDF, PTFE, ECTFE, PFA, or MFA. Moreover, this method is not restricted to any particular form of fluoropolymer resin. Powders (e.g., having diameters of from about 10 nm to about 0.1 mm), beads (e.g., having diameters of from about 0.1 to about 0.5 mm), films, filaments, and fibers can be employed in place of the 12" x 2" FEP sheet.

Example 2 -- Preparation and Characterization of V_2O_5 in Polyethyleneterephthalate

The same experiment as described in Example 1 was performed using a piece of polyethyleneterephthalate ("PET"), which is a polyester containing only aliphatic carbon and ester functionality. Upon exposing the PET in the same manner as that described in Example 1, the same observations were made. That is, initially the PET film was transparent and within a few hours turned to yellow green. Although the color to the eye was slightly different, the UV-vis results showed a

similar spectrum as that observed for the FEP. XPS, on the other hand, showed a binding energy of ca. 517.5 eV which is consistent with V_2O_5 . This further supports the results in Example 1, which indicated that the vanadium was somehow complexed to the fluorine functionality thereby increasing its XPS binding energy. These results suggest that the electronic state of the inorganic material in the free volume of the polymer matrix can be influenced by the functional groups contained in the polymer making up the polymer matrix.

Example 3 -- Preparation and Characterization of Fe_2O_3 in Polytetrafluoroethylene-co-hexafluoropropylene

A piece of FEP polymer was treated exactly in the same manner as that described in Example 1, except that instead of using $V(O)Cl_3$, 1 ml of $Fe(CO)_5$ was vacuum transferred to the flask containing the FEP. The temperature and treatment time was identical to those described in Example 1. Upon removal the film turned deep orange. XPS and UV-vis results indicated the formation of Fe_2O_3 . A slight shift to higher binding energy in the XPS for the Fe_2O_3 -FEP material indicated that the iron was, in some manner, electronically coupled to the fluorine functionality in the FEP.

In accordance with this invention the materials are contemplated as useful light and electromagnetic radiation shields or filters. Examples 1-3 showed that vanadium and iron macromolecular networks can be formed within FEP and PET. Both of FEP and PET are lightweight and flexible. Additionally, the FEP material is extremely resistant to weathering and is chemically inert. Contact angle experiments were performed on the material made in Example 1 and showed negligible change in the surface properties of the FEP fluoropolymer (i.e., the water contact angle was still greater than 90 degrees), indicating that the inherent resistance to weathering and inertness to solvents and chemicals for this fluoropolymer were left intact. Thus, Examples 1-3 show that the methods of the present invention can be used to make flexible, lightweight, materials which have UV radiation absorbance and which have surfaces which resist weathering, fouling, and chemical degradation.

Example 4 -- Preparation and Characterization of TiO₂ in Polytetrafluoroethylene-co-hexafluoropropylene

In Examples 1-3, the vanadium and iron inorganic networks imparted a visible hue to the polymeric materials, which would be undesirable in applications requiring high transparency in the visible region of the light spectrum. To provide a material which is transparent to visible light but which blocks or absorbs large amounts of UV radiation, another inorganic complex, based on titanium, can be used.

A piece of FEP polymer was treated exactly in the same manner as that described in Example 1 except that instead of using V(O)Cl₃, 1 ml of TiCl₄ was vacuum transferred to the flask containing the FEP. The temperature and treatment time were identical to those described in Example 1. Upon removal, the film was totally transparent to the naked eye and was never observed to change. XPS and UV-Vis results indicated the formation of TiO₂, and a slight shift to higher binding energy in the XPS was observed, which indicated that the titanium was in some manner electronically coupled to the fluorine functionality in the FEP.

As in Example 1, the FEP sheet used here can be replaced with other fluoropolymer resins (e.g., PVDF, PTFE, ECTFE, PFA, or MFA) or with other polymer forms, such as powders (e.g., having diameters of from about 10 nm to about 0.1 mm) or beads (e.g., having diameters of from about 0.1 to about 0.5 mm).

Example 5 -- Preparation, Characterization, and Use of WO₃ in Polytetrafluoroethylene-co-hexafluoropropylene

Although titanium, vanadium, and iron are good UV radiation shields, it would also be of use to form a network of a high Z number (i.e., high density or heavy weight) metal. High Z number metals are efficient for not only blocking UV radiation but are more often used for shielding high energy UV and x-radiation. Tungsten belongs to this class of metals. However, no metallic complex of tungsten exists in a liquid form capable of being boiled into a gas phase. In view of this, a different method for self-assembling of a tungsten heteropolycondensate into polymers was developed.

The method described here illustratively uses an FEP sheet. However, the method can be applied equally well to other fluoropolymers (e.g., PVDF, PTFE,

ECTFE, PFA, or MFA) and to other resin forms, such as powders (e.g., having diameters of from about 10 nm to about 0.1 mm) or beads (e.g., having diameters of from about 0.1 to about 0.5 mm).

5 A 2" x 2" piece of FEP polymer was placed in a 100 ml round bottom flask along with 100 mg of $W(CO)_6$. The flask was connected to a vacuum line and then pumped down to less than 10 mTorr pressure. Next, the flask was heated to 75°C, which, at 10 mTorr pressure, was sufficiently high to initiate the sublimation of the $W(CO)_6$ and to create a vapor phase of the tungsten complex within the flask. After 1 hr, the FEP material was removed and placed under ambient air conditions for 2
10 hrs. UV-Vis experiments showed a large absorbance band at 228 nm ($A = 3.4$) with a smaller absorbance band at 288 nm ($A = 0.4$), indicating the formation of a complex inside the FEP. The sample was highly transparent in the visible region of the spectrum. Unlike the vanadium, titanium, and iron samples used in Examples 1-4, not only did this particular tungsten complex need to be sublimed instead of
15 boiled, it also possessed carbonyl ligands which are relatively stable compared to those on the metal complexes used in Examples 1-4. Thus, after obtaining the UV-Vis spectra, the FEP sample was placed under a high energy, broad band ultraviolet source centered at 254 nm in the presence of air for 1 hr. The carbonyl ligands associated with this tungsten compound are known to be photoactive under UV
20 radiation.

After exposing the sample to the UV lamp, several changes were observed in the UV-vis spectrum. The absorbance at 288 nm decreased slightly to $A = 0.37$; the band at 228 nm decreased from $A = 3.4$ to 1.1; and, at 190 nm (which is the limit of the instrument's capability with respect to measuring low wavenumber
25 absorbance values), the absorbance changed from 0.4 (before UV irradiation) to 1.5 (after UV irradiation). It is believed that this indicates that the complex formed after irradiation had a greater propensity for shielding higher energy radiation (i.e., radiation at lower wavenumbers) and would be quite useful as such as a flexible, visibly transparent material. WO_3 is well known for its ability to shield x-radiation.
30 It was observed that, after having been diffused into the FEP, the tungsten compound absorbed in the mid UV range, as would be expected had the tungsten carbonyl, after having been diffused into the FEP, retained either all or a portion of its original carbonyl ligands. Macromolecular tungsten complexes are known for their ability to

shield high energy radiation, which is what was observed after the carbonyls were removed by UV radiation in the presence of water- or oxygen-containing air. This supports the proposition that treatment with UV radiation in the presence of air produced hydrolyzed and/or oxidized form of tungsten which then self-assembled with neighboring hydrolyzed or oxidized tungsten to form a macromolecular complex.

Example 6 -- Stability of Polycondensate Networks Incorporated in FEP Via Exposure To Supercritical CO₂ Environments

6" x 6" pieces of FEP were treated in the same fashion as the FEP treated in Example 1. After these FEP films were metallated with V₂O₅ as described, the films were placed into a high pressure stainless steel vessel. The vessel was then charged with 2500 psi of CO₂ gas at 40 °C. These conditions result in the formation of a supercritical CO₂ environment under which FEP is known to swell. Swelling of FEP films under these conditions allows for the rapid exchange of CO₂ with weakly bonded molecules contained within the free volume of the polymer. The FEP samples in this example were left under these conditions for 72 hrs. UV-vis analysis of the FEP films (after 72 hrs) indicated only negligible V₂O₅ loss (less than 10%) and suggested that the network formed within the polymer matrix was either: (1) permanently entrapped inside the polymer due to physical interactions between the polymer chains with formed heteropolycondensate macromolecules, and/or: (2) permanently entrapped inside the polymer due to chemical or electronic interactions between the functional groups contained within the polymer and the atoms and/or functional groups of the heteropolycondensate macromolecular network. The stability demonstrated in this example makes these materials good candidates for use as heterogeneous catalysts utilized under supercritical process conditions.

Likewise the experiment was performed using small 50 micrometer beads of the copolymer ethylenechlorotrifluoroethylene ("ECTFE") which also contained macromolecular networks of V₂O₅. These materials were prepared also using the procedure described in Example 1.) Again, there was no observed loss of the V₂O₅ inorganic material after exposure to the supercritical conditions. It is believed that these experiments show that the macromolecular inorganic networks can be permanently stabilized into polymer matrices either by coordinating with functional

groups (like the fluorine and/or chlorine groups contained within FEP and ECTFE) or by entanglement within chains contained in the amorphous regions of the polymer where the inorganic networks are formed. Furthermore, because these materials are stable under supercritical conditions, they can be used as heterogeneous catalysts in supercritical fluid reactors, such as those described in Patchornick, Winslow, and Cunningham, which are hereby incorporated by reference.

Example 7 -- Stability of Polycondensate Networks Incorporated in PTFE, ECTFE, PVDF, PMMA, PP, PS, and PVDF Via Exposure To Supercritical CO₂ Environments

2" x 2" pieces of PTFE, ECTFE, PVDF, polymethylmethacrylate ("PMMA"), polypropylene ("PP"), polystyrene ("PS"), and polyvinylidene fluoride ("PVDF"), were treated in the same fashion as the FEP treated in Example 1. After these films were metallated with V₂O₅, they were first analyzed by UV-vis spectroscopy as described previously, the films were then placed into a high pressure stainless steel vessel. The vessel was then charged with 2500 psi of CO₂ gas under ambient temperatures. The samples were left under these conditions for 72 hrs. UV-vis analysis of these films (after 72 hrs) indicated only negligible V₂O₅ loss (less than 10%) and suggested that the network formed within the polymeric matrices were either: (1) permanently entrapped inside the polymer due to physical interactions between the polymer chains with formed heteropolycondensate macromolecules, and/or: (2) permanently entrapped inside the polymer due to chemical or electronic interactions between the functional groups contained within the polymer and the atoms and/or functional groups of the heteropolycondensate macromolecular network. The stability demonstrated in this example makes these materials good candidates for use as heterogeneous catalysts which may be utilized under supercritical conditions.

Example 8 -- Heterogeneous Catalysis of SO₂ to SO₃

A 3" x 18" piece of a 1.0 mil thick sample of FEP was treated in the same fashion as the FEP material treated in Example 1. The piece of metallated (V₂O₅) FEP was then placed into a 100 ml stainless steel reactor which was then charged with 4 atmospheres of O₂ and 1 atmosphere of SO₂. The vessel was then heated to

70 °C for 24 hrs. After this treatment, the vessel was opened, and the FEP was removed. Next, a calibrated amount of deionized H₂O was added to the vessel to convert any SO₃ which was formed during the catalytic reaction to H₂SO₄. Using a pH meter to measure the resultant acidity of the added deionized H₂O, the pH was determined to be 1.8. Calculations involving the initial concentration of SO₂ and the resultant pH of the known amount of added H₂O determined that greater than 90% of the SO₂ was catalytically converted to SO₃. Subsequent analysis (by UV-Vis spectroscopy) of the metallated FEP showed no detectable loss of V₂O₅, thus indicating the stability of the V₂O₅ macromolecular network within the FEP film during the catalytic procedure.

Molecular transformations which utilize V₂O₅ as an oxidation catalyst for converting SO₂ to SO₃ often require reaction temperatures greater than 500 °C, which indicates that the material used here may have enhanced capabilities with respect to its operation as a heterogeneous catalyst. Further, the results from this example, though only illustrative, demonstrate the utility of V₂O₅ and other metallic complexes interpenetrated into inorganic-organic materials as oxidation catalysts.

Example 9 -- EMI Shields, UV Light Filters, and Photolithographic Masking

Materials

Examples 1-8 showed materials which absorb UV and x- radiation at levels which may be useful for coatings or films which inhibit and/or attenuate radiation from penetrating these films while in contact with UV, extreme UV, and X-ray sensitive materials. As one example, this is demonstrated by the UV-Vis absorbances throughout the UV-Vis spectrum range (i.e., 190 nm - 400 nm) of greater than 2.0 absorbance units (i.e., 99% UV absorbance) for films infused with vanadium or titanium. Further, these results, when taken together with the results which indicate the formation of macromolecular networks of inorganic/metallic complexes in the composites of the present invention, suggest that the composites are useful for either absorbing electromagnetic radiation, reflecting electromagnetic radiation, or transforming various electromagnetic radiation into electrical current (i.e., acting as an electromagnetic interference ("EMI") shield). Since conventional photolithographic and imaging processes require polymeric photoresist materials capable of blocking these different types of radiation during exposure steps, the

composites of the present invention can be used as masks in such conventional photolithographic and imaging processes. For Example, U.S. Patent 5,387,481 to Radford et al. ("Radford"), which is hereby incorporated by reference, describes a vanadium oxide which can act as a switchable shield for blocking electromagnetic radiation. The vanadium oxide compound used in Radford, when heated, is said to exhibit a marked and rapid transition from a dielectric material, which is transparent to electromagnetic radiation, to a metallic, electromagnetic radiation shield, which is impervious to electromagnetic radiation. In Radford, the vanadium oxide material is applied as a thin film to a solid substrate. In the present invention the vanadium oxide can be initially incorporated into an a polymer matrix to produce a composite according to the present invention. Upon heating, the vanadium oxide would be transformed from a material which is transparent to electromagnetic radiation to one which effectively blocks such radiation. This example is only illustrative: other composites of the present invention, particularly those which contain conductive macromolecular networks (e.g., those containing Ti, Fe, Pb, and Au) can act as efficient blockers of electromagnetic radiation, such as UV, extreme UV, and x-radiation.

Example 10 -- Battery and Fuel Cell Separators

Example 1, above, showed that molecules of hydrofluoric acid ("HF") and ions generated therefrom could interpenetrate into a fluoropolymeric material like FEP and PET which contained a vanadium macromolecular complex. This was demonstrated by UV-Vis data which showed the disappearance of certain molecular absorbances as well as by the naked eye which showed that the material turned from yellow-orange to a totally transparent material when placed into the HF solution. Further these materials were observed to change back to a yellow-orange color, with no detectable loss of the vanadium complex, upon removing the HF solution and exposing the material to air. This demonstrates that, even after formation of the composite material, both gas phase and liquid phase molecules and ions can be transported through the material and can react or coordinate with the vanadium (or any other metal or inorganic complex) contained within the free volume of the polymer matrix in a reversible fashion. Further, as described above, many of the inorganic materials incorporated within the free volume of the polymer matrix

contain catalytically active metals or metals which can act as good redox materials (i.e., metals which can donate or accept electrons from charged ions or molecules). The ability of gases and liquids to diffuse into free volumes containing catalysts or redox materials suggests that the composites of the present invention are useful as electrodes and separation materials, such as in battery and fuel cell applications.

For example, U.S. Patent 5,470,449 to Bachot et al., which is hereby incorporated by reference, describes the preparation of microporous diaphragms adapted for wet-consolidation with composite cathodes for use in electrolytic cells. These microporous diaphragms include a sintered fluoropolymer microporous fibrous sheet material containing from 3% to 35% by weight of fluoropolymer binder and from 0% to 50% by weight of a uniformly distributed gel of an oxohydroxide (i.e., a heteropolycondensate) prepared from a metal like Ti or Si.

The methods of the present invention can be used to make a composite of a fluoropolymeric matrix material having macromolecular networks of metal oxohydroxides incorporated therein. For example, Ti oxohydroxides can be networked into FEP films as described in Example 4. As a further example, a macromolecular network of Si oxohydroxide was also incorporated into an FEP film by first placing a 12" x 2" piece of FEP into a 100 ml round bottom flask, connecting the flask to a vacuum line, pumping the flask down to less than 10 mTorr pressure, and vacuum transferring about 1 ml of SiCl_4 to the flask. The flask was then closed and heated to about 75 °C under vacuum so that a gas phase of SiCl_4 filled the entire volume of the flask for 1 hr. The SiCl_4 was then vacuum transferred off the FEP polymer, and the flask was opened to ambient air. Upon exposure to air, the SiCl_4 , which was incorporated into the FEP film, underwent hydrolysis, which resulted in the formation of a macromolecular network of Si oxohydroxide, as confirmed by IR spectroscopy which measured Si-O absorbance at about 1025 cm^{-1} .

The composites of the present invention can also be used in the electrolytic cells and fuel cells described in U.S. Patent 5,512,389 to Dasgupta et. al. ("Dasgupta"), which is hereby incorporated by reference. Dasgupta describes the use of a solid polymer electrolyte in a non-aqueous, thin film rechargeable lithium battery. They can also be used in electrochemical cells in place of the halogenated (e.g., fluoropolymeric) separator material used in the electrochemical cells described in U.S. Patent 5,415,959 to Pyszczyk et al., which is hereby incorporated by

reference. As a further illustration, the composites of the present invention can be used as a solid polymer electrolyte in place of the solid polymer electrolyte (prepared by bonding catalytic metals to solid polymeric materials) used in U.S. Patent 5,474,857 to Uchida et al., which is hereby incorporated by reference.

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Example 11 -- Electrically Conductive Flexible Materials for Optoelectronics

Many of the heteropolycondensates formed within the polymeric matrices using the methods of the present invention have electrical and electrical and/or ionic conductivity properties which make them useful in technologies which require flexible materials having electrically or ionically conductive and/or antistatic characteristics. For example, MacDiarmid et. al., Proc. Materials Research Society, Boston, MA (November 1995) and copending U.S. Patent Application 08/401,912, which are hereby incorporated by reference, describe the use of conducting polymers adhered to flexible substrates as flexible electrode materials in the construction of electro-optical devices. By appropriate choice of a flexible polymer matrix, the methods of the present invention can be used to produce conducting composites which can be used in such electro-optical devices.

For example, a 4" x 4" sheet of FEP was placed into a 100 ml round bottom flask. The flask was connected to a vacuum line and then pumped down to less than 10 mTorr pressure. Next, about 1 ml of pyrrole was vacuum transferred to the flask, and the flask was closed and heated to about 75 °C under vacuum so that a gas phase of pyrrole molecules filled the entire volume of the flask for 1 hr. The pyrrole was then vacuum transferred off the FEP polymer, and the flask was opened to ambient air. The sample was then placed into an oxidizing solution of HNO₃ for 12 hrs. Upon removal, the film had acquired a grey tint. Inspection by UV-Vis confirmed the formation of a polypyrrole network within the FEP matrix.

As a prophetic example, heteropolycondensates of indium and tin, known as indium tin oxide ("ITO"), when evaporated onto a variety of substrates, are used commercially as a transparent conducting film. These ITO films are used as electrode materials in the construction of many electro-optical devices (e.g., liquid crystal based flat panel displays). The methods of the present invention can be used to produce conductive thin films which can be used in place of the ITO films in such electro-optical devices. To illustrate this aspect of the present invention, a 4" x

4" sheet of FEP can be placed into a 100 ml round bottom flask. The flask is then connected to a vacuum line and pumped down to less than 10 mTorr pressure. Next, about 1 ml of triethylindium and about 1 ml of SnCl_4 is vacuum transferred to the flask. The flask is then closed and heated to about 75 °C under vacuum so that a gas phase of both the triethylindium and SnCl_4 fills the entire volume of the flask for 1 hr. The triethylindium and SnCl_4 are then vacuum transferred off the FEP polymer, and the flask is opened to ambient air. Upon exposure to air, both the triethylindium and the SnCl_4 which are incorporated into the FEP film undergoes hydrolysis, which results in the formation of a macromolecular network of ITO.

Example 12 -- Electronic Imaging Applications

Rajeshwar, which is hereby incorporated by reference, describes the use of polymer films containing nanodispersed catalyst particles of electronically conductive polymers containing polypyrrole, polyaniline, and polythiophene in imaging applications. The polymer films described in Rajeshwar can be replaced by the composites of the present invention to produce materials useful in imaging.

For example, polypyrrole containing composites can be prepared and treated in the following manner. A polypyrrole deposition solution was prepared by mixing 100 ml of a solution containing 0.6 ml of pyrrole in deionized water together with 100 ml of a solution containing 3.4 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.98 g anthraquinone-2-sulfonic acid sodium salt monohydrate, and 5.34 g 5-sulfosalicylic acid dihydrate in deionized water. The polypyrrole films were then deposited onto a polyethyleneterephthalate ("PET") film measuring 2" x 2" by immersing the PET film for 5 min into a magnetically stirred polypyrrole deposition solution. The PET having a film of polypyrrole thereon was then ultrasonicated in methanol, rinsed with deionized water, and dried under N_2 . The film of polypyrrole on PET was then treated in the same fashion as the FEP treated in Example 1 (to incorporate a V_2O_5 heteropolycondensate macromolecular network). After the film containing VOCl_3 was exposed to air to facilitate hydrolysis, it was examined by UV-Vis spectroscopy, and the spectrum was compared to the UV-Vis spectrum initially obtained from the polypyrrole film which was deposited onto the PET material. The comparison of UV-Vis spectra showed differences which substantiated the incorporation of V_2O_5 into the conducting layer of polypyrrole.

In an alternative method, a 4" x 4" film of FEP was treated as described in Example 1 (i.e., incorporated with a V_2O_5 heteropolycondensate macromolecular network). The film was then placed into a 100 ml round bottom flask, and the flask was connected to a vacuum line and pumped down to less than 10 mTorr pressure. Next, about 1 ml of pyrrole was vacuum transferred to the flask, and the flask was then closed and heated to about 75 °C under vacuum so that a gas phase of pyrrole molecules filled the entire volume of the flask for 1 hr. The pyrrole was then vacuum transferred off the FEP polymer, and the flask was opened to ambient air. It was observed, with no further treatment, that the film had acquired a grayish tint normally associated with polypyrrole. UV-Vis spectroscopy confirmed that the pyrrole which had diffused into the FEP material had been oxidized by the V_2O_5 contained in the film prior to exposure to the pyrrole. The UV-Vis spectroscopy also confirmed that the pyrrole molecules had been oxidatively converted to a polymeric macromolecular network of polypyrrole.

The composites of the present invention can also be used as electroconductive imaging elements, such as those used in high speed laser printing processes which utilize electrostatography. For example, the composite of the present invention can be used as a replacement for the electroconductive imaging element described Anderson I, which is hereby incorporated by reference. Suitable composites for use as electroconductive imaging elements include the materials described in Examples 1 and 2 which incorporate V_2O_5 macromolecular networks into both PET and FEP. Using the UV-Vis measurements obtained in Examples 1 and 2, it was calculated that both the PET and the FEP materials contained greater than 40 milligrams of V_2O_5 per square meter. Using processes described herein, the concentration of inorganic and/or organic macromolecular networks formed within the polymer matrix can be reduced to the levels of V_2O_5 disclosed in Anderson I, e.g., about 3 mg per square meter.

Example 13 -- Methods for Controlling the Concentration of Inorganic and/or Organic Heteropolycondensates in Polymeric or Inorganic-organic Matrices

All of the above examples describe methods for making composites which contain polymers and inorganic-organic hybrid materials having macromolecular networks of polymers and/or macromolecular networks of inorganic polycondensates

incorporated within their matrices in regions referred to and defined in the specifications of this application as free volume. The methods used and described in previous examples demonstrate the ability to conveniently diffuse inorganic and/or organic molecules into free volume spaces inherent in any polymeric or inorganic-organic hybrid material and, then, to convert these molecules to large macromolecular networks or macromolecular polycondensates. These free volumes can be thermally controlled so that the concentration or total amount of organic network or inorganic polycondensate which is incorporated into the total volume of the template polymeric or inorganic-organic hybrid material can also be controlled. Essentially, as one increases the temperature during the initial step of diffusing any inorganic, metallic, or organic molecule into a given polymer or inorganic-organic hybrid material, one also increases the free volume into which these materials can diffuse (providing the temperature is below the thermal decomposition temperature of the polymer or inorganic-organic hybrid material and the decomposition temperature of the starting inorganic, metallic, or organic molecule). To illustrate this phenomenon, a series of FEP materials were exposed to VOCl_3 and subsequently hydrolyzed to V_2O_5 in the same manner as that described in example 1, except that they were initially exposed to the VOCl_3 vapor at different temperatures. By measuring the UV-Vis absorbance at 225 nm it was observed that at 27 °C, $A=0.14$; at 40 °C, $A=0.31$; at 60 °C, $A=1.05$; at 70 °C, $A=1.63$; at 80 °C, $A=2.5$; and at 90 °C, $A=3.14$. These results demonstrate that control over the concentration of introduced macromolecular material can be facilitated by the methods described herein.

Example 14 -- Localization of the Macromolecular Network

This example establishes that the macromolecular networks form primarily in the free volume of the polymer matrix. As described above, conventional methods for making inorganic-organic hybrids involve either: (1) solubilizing an inorganic precursor capable of forming a macromolecular network within a polymeric material with a solvent appropriate for solubilizing both the starting polymer and the starting inorganic molecule, adding a hydrolyzing agent, and drying and/or curing the mixture to form a composite material, (2) adding an inorganic precursor which is capable of forming a macromolecular network along with a

hydrolyzing agent to a molten polymeric material and drying and/or curing the mixture to form a composite material, or (3) using supercritical fluids. In the first two cases, the resulting material contains both the starting polymeric material and an inorganic heteropolycondensate. Due to mixing and curing, the resulting material
5 dries and/or cures simultaneously to form a material dependent on the presence of both the initial starting polymeric material and the formed heteropolycondensate. In other words, the polymer's final physical (i.e., morphological), electrical, and chemical properties are substantially changed from that of the starting polymeric material. Further, fine control over the resulting properties of the composite material
10 is difficult and requires extensive trial and error, which may show that the desired property is not permitted by the technique utilized. In the third case, use of supercritical conditions gives rise to a variety of disadvantages, such as those discussed above.

In the composites of the present invention, the polymeric or inorganic-
15 organic hybrid materials act only as templates to support the formation of macromolecular organic or inorganic polycondensate networks within their free volume. This not only can preserve many of the physical, electrical, and chemical properties of both materials, but also allows one to controllably enhance desired properties of either the polymeric matrix material or the incorporated
20 macromolecular network (e.g., catalytic activity).

For example, preparation of an inorganic-organic hybrid porous filter material using methods described in the prior art requires that the material be first melted or dissolved and then mixed with at least an inorganic precursor. This mixture must then be dried and/or cured so that it has similar porosity to that of the
25 starting polymer. This is difficult if not impossible due to the new nature of the hybrid material melt or solvated material. In contrast, by treating the same porous filter material using methods of the present invention, the desired characteristics can be imparted to the pre-formed filter material without changing the physical pore size or the surface morphology of the filter material.

30 Example 13 shows that the composites of the present invention contain organic macromolecules and heteropolycondensate networks within the free volume of polymeric and inorganic-organic hybrid materials. To further characterize the composites of the present invention, thermal analyses were conducted on a variety of

materials prepared by the methods of the present invention. More particularly, thermal decomposition ("Td") and differential scanning calorimetry ("DSC") studies were performed on two separate films of ECTFE containing heteropolycondensate networks of titanium and vanadium respectively. The films were prepared using the procedures described in Examples 1,2 and 4. Results showed only negligible change in the material's decomposition temperature and no change in their degree of crystallinity (i.e., no change in the original polymer's morphology). Likewise, using the procedures described in Examples 1-3, two films of perfluorinated alkoxy resin were treated so that one contained a heteropolycondensate network of titanium and the other vanadium. These samples also showed no change in decomposition temperature or degree of crystallinity. Finally, two films of FEP were likewise treated and also showed negligible changes with respect to the Td and DSC measurements.

These results indicate that the macromolecular networks form along the free volume spaces of the polymeric matrix materials and preserve the morphology of the inherent structure (i.e., crystallinity and physical morphology) of the polymeric matrix.

Example 15 -- Increasing and/or Stabilizing the Mechanical Strength of Materials

Example 8 showed how the chemical functionality and the electronic nature of a polymeric matrix could act to enhance the catalytic activity of a metal center contained within a macromolecular vanadium polycondensate (i.e., a V_2O_5 network incorporated into a fluoropolymeric material). Conversely, the functionality contained in a heteropolycondensate network incorporated into a polymer or inorganic-organic hybrid material can be made to influence the chemical, thermal, and/or mechanical strength of the matrix material. Many polymers are well known to physically or chemically degrade either thermally, chemically, or through the exposure to actinic radiation. This ultimately leads to loss in the material's mechanical strength. For example, thermal mechanical analysis ("Tm") of ECTFE shows that, when it is exposed to temperatures of or about 250 °C, mechanical strength significantly decreases (i.e., the polymer melts and begins to flow).

To demonstrate that the functionality contained in a macromolecular network disposed in a polymer matrix's free volumes can influence the chemical,

thermal, and/or mechanical strength of the polymeric matrix material, two 2" x 2" pieces of ECTFE were treated in the same manner as were the FEP samples described in Examples 1,2 and 4. One piece of ECTFE contained a macromolecular network consisting of the heteropolycondensate V_2O_5 , and the other contained a heteropolycondensate of TiO_2 . Both materials were analyzed via thermal mechanical analysis, which measures mechanical strength as a function of temperature. In the case where the ECTFE film was incorporated with V_2O_5 , no change was observed in its mechanical strength as a function of increased temperature, indicating little or no interaction between the incorporated V_2O_5 and the ECTFE polymer upon heating. In contrast, Tm measurements on the TiO_2 incorporated ECTFE showed an interaction of the TiO_2 polycondensate network with the ECTFE after thermally treating the composite which resulted in no observable loss of the ECTFE's mechanical strength up to temperatures at or around 400 °C. This was an increase of over 125 °C compared to the untreated ECTFE, which indicates that the TiO_2 network interacts during heating (but not after the initial formation of the composite) with the ECTFE and acts to stabilize the structure which in turn preserves and extends the ECTFE's mechanical strength at temperatures 125 °C above its normal usefulness.

Example 16 -- Anti-static Materials Used as Photographic Elements and Support Layers.

The composites of the present invention can be used as anti-static materials for use as photographic elements and support layers. U.S. Patent 5,284,714 to Anderson et al. ("Anderson II"), which is hereby incorporated by reference, describes photographic support materials comprising an anti-static layer and a heat thickening barrier layer. The anti-static layer comprises a V_2O_5 film applied to a material which is overcoated with a heat thickening polyacrylamide layer. The composites of the present invention can be used in place of the antistatic layer used in Anderson II. For example, instead of applying a thin layer of polyacrylamide on top of an anti-static V_2O_5 film, one can simply incorporate the anti-static V_2O_5 directly into the polyacrylamide using the methods of the present invention.

Similarly, U.S. Patent 5,366,544 to Jones et al. ("Jones"), which is hereby incorporated by reference, describes the use of an anti-static layer used as a photographic imaging element prepared by mixing V_2O_5 into a polymeric cellulose

acetate binder. Using the methods of the present invention, V_2O_5 can be incorporated directly into a cellulose acetate binder. This material can then be used in place of the anti-static layer described in Jones.

Finally, U.S. Patent 5,439,785 to Boston et al, ("Boston"), which is hereby incorporated by reference, describes photographic elements comprising anti-static layers of V_2O_5 , epoxy-silanes, and sulfopolyesters. Using the methods of the present invention, V_2O_5 can be readily incorporated into sulfopolyesters as well as epoxy-silanes, and these materials can be used as antistatic layers in the photographic elements disclosed in Boston.

Example 17 -- Infusion of Stabilized Metal Species Into a Preformed Polymeric Material

A 2" x 2" piece of FEP polymer film was placed into a glass tube with 100 mg of ferrocene, and the tube was connected to a vacuum line and pumped down to less than 10 mTorr pressure. Next, the glass tube containing the FEP film and ferrocene was sealed under vacuum and immersed in an oil bath at 80 °C, which, at 10 mTorr pressure, is sufficiently high to sublime and produce a gas phase of ferrocene within the reaction tube. After 1 hr, the FEP was removed from the reaction vessel and thoroughly rinsed in toluene for 30 min. In this example the infused ferrocene molecules do not form macromolecular networks, and the stability of the ferrocene molecules depends on their ability to complex or interact with the fluorine functionality contained within the FEP polymer. Incorporation of the ferrocene was confirmed via analysis by UV-Vis spectroscopy.

Example 18 -- Infusion of Pi-allyl Metal Complexes Into Preformed Polymeric Materials

A polymer film can be first placed along with 100mg of pi-allyl complex into a reaction vessel which is subsequently attached to a vacuum line. The vessel is pumped down to less than 10 mTorr at -196 °C. The evacuated vessel is then heated to 80 °C for 1 hr. The polymer film is removed from the reaction vessel and then exposed to an atmosphere of H_2 gas which converts the allyl complex contained within the polymer to a reduced metal form which is stabilized within the polymeric

material with con-current release of propane gas out of the polymeric film.

Example 19 -- Catalytic Oxidation of Methanol and o-Xylene

100 mg of MFA resin (beads having diameters of about 0.5 mm) were
5 infused with vanadium (about 1%-2% vanadium, by weight) using the method set
forth in Example 1. The infused MFA resin was then placed in a stainless steel
vessel. After sealing the vessel, gas ports were used to fill the vessel with a mixture
of 20% oxygen and 80% helium at atmospheric pressure. Next, 5-10 microliters of
methanol was introduced, and the vessel was heated to 60°C for two hours. The
10 product was analyzed using gas chromatography, and the conversion of methanol to
both formaldehyde and formic acid were indicated.

The same experiment was performed using o-xylene instead of methanol.
Analysis by both gas chromatography and infrared spectroscopy indicated that the
o-xylene was selectively oxidized to phthalic anhydride.

15 Infusing titanium into fluoropolymer resins should also produce a good
heterogeneous catalyst, particularly well-suited for catalyzing selective oxidation
reactions as well as for promoting polymerization of alkenes into their respective
olefinic polymers. In some cases, the oxidation reactions may require a co-reductant,
such as peroxides (e.g., hydrogen peroxide or benzoyl peroxide) or, as another
20 example of many co-reductants, iodosobenzene, which is commonly used in the
epoxidation of olefins in the presence of metalloporphyrins.

Example 20 -- Antifouling Compositions

Vanadium was infused into both MFA and FEP fluoropolymers using the
25 method described in Example 1. The infused MFA and FEP were films having
thicknesses of 3 mils and 8" x 10" geometry. These films plus two reference MFA
and FEP films (containing no vanadium) were then epoxied to a 4' x 3' sheet of
plywood which was subsequently placed into an intercoastal marine waterway on the
Gulf of Mexico side of Florida near Sarasota for two months. When, after two
30 months, the plywood sheet was removed from the water, the entire board was
encrusted with barnacles and other marine crustaceans. Upon exposing the board to
a mild spray of water, however, almost all of the crustaceans were removed from the

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MFA and FEP films which were infused with vanadium. Removal of the crustaceans from the reference MFA and FEP was approximately only 50%, and the crustaceans attached to the plywood were left 100% intact after the water spray test.

To establish whether vanadium leached from the MFA and FEP sheets, the vanadium-infused MFA and FEP sheets were subjected to hot nitric acid solutions for over 72 hours. Analysis of the solutions by inductively coupled plasma ("ICP") atomic absorption spectroscopy and UV visible spectroscopy showed the absence of any vanadium complex therein. Thus, no leaching of vanadium was observed at detection limits of 1 ppb, suggesting that the vanadium complex inside of the MFA and FEP was left intact.

These results demonstrate that the antifouling coatings of the present invention are not deposited into the environment, in contrast to conventional antifouling marine coatings which operate primarily by sloughing off heavy metals or other toxic materials from the surface onto which they are coated. Therefore, the antifouling coatings of the present invention are particularly advantageous in environments which are sensitive to the toxic effects of heavy metals. Furthermore, because the composites of the present invention do not operate by releasing the active ingredient (e.g., metal), it is expected that the composite will have a much greater antifouling lifetime.

Example 21 -- Modification of FEP Before and After Infusion of FEP With SiCl₄

Modified FEP. FEP was modified using a H₂/MeOH plasma as described hereinabove. For this experiment the FEP was modified using a 90 second exposure which results in a nominally modified material (i.e., only 2.8% oxygen and about a 3:1 ratio between the C-F₂ and the modified C-OH functionality measured and observed in the ESCA carbon 1s region).

Modified FEP + SiCl₄ Infusion. This sample was produced using a 90 second radio frequency glow discharge comprised of H₂ and MeOH as described hereinabove as the preferred method of modification. The infusion was carried out by placing a 4 cm x 6 cm, 2 mil thick film of the modified FEP into an evacuated vessel containing approximately 1.0 g of SiCl₄ evacuated to less than 10 mTorr and reacting for 1 hr at room temperature. After removing the FEP sample from the

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infusion vessel the FEP was ultrasonically cleaned in H₂O for 30 min to both hydrolyze the SiCl₄ to the polycondensate (e.g., -(SiO_x-O-SiO_x)-) and to eliminate any of the formed silicate not covalently bonded to the surface or not permanently infused into the material. Subsequent analysis by ESCA showed that the surface had 1.8% silicon and that the oxygen % increased from 2.8% (measured on the modified non-infused FEP) to 7.2%. These results indicate that the silicate was both formed not only within the bulk but also, unexpectedly, at the surface. Table 2 lists the ESCA results for the unmodified FEP infused with SiCl₄. When infusion was carried out on unmodified FEP only, 0.3% Si and 2.2% oxygen were measured at the FEP surface. Thus, by first modifying the FEP, one can obtain not only a fluoropolymer having bulk infused metal oxide but also a material having an overcoating of the silicate (metal oxide) at the interface of the FEP material. This silicate overcoating is useful for bonding metals, metal oxides, polymers, biological molecules, and phosphorescent and/or luminescent materials.

Inspection by X-ray Photo-Electron Spectroscopy (ESCA or XPS) of the oxygen 1s region of the infused modified FEP showed two bands: one at ca. 536.5 and one at ca. 533.5. The 533.5 band corresponds to the surface residing silicate. The band observed at ca. 536.5 is unusually high and is indicative of the oxide of the silicate contained within the infused highly electronegative FEP bulk. This is consistent with the Si2p ESCA results which show only one band centered at ca. 102.8 eV, which is consistent with what one would observe for a silicate.

Combining these results indicates that the species of silicate formed both within and at the interface of the fluoropolymer are the same in chemical nature but that the silicate formed within the fluoropolymer matrix is influenced by the surrounding fluoropolymer electronegativity which results in a bulk and surface silicate having different electronic characteristics.

Unmodified FEP Infused with SiCl₄. Unmodified FEP was infused with SiCl₄ using the identical conditions described above for the infusion of SiCl₄ into modified FEP. The subsequent hydrolysis of the SiCl₄ to the silicate takes place, and, as can be observed from Table 2, only a very small concentration of the silicate is observed at the interface. The only observation made on this material pertains to the oxygen 1s region of the ESCA spectrum, which shows the bands at 536.5 and

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533.5. The bands at 536.5 and 533.5 are consistent with the previous discussion which explains these two distinct ESCA oxygen 1s bands as being similar in chemical nature (i.e., a silicate oxide) but different in electronic nature (due to silicate residing in the bulk of the fluoropolymer versus the silicate residing on the surface of the FEP). These results are similar to those reported for the silicate infused modified FEP material as described above except that the band associated with the oxygen present at the surface is much larger in the case where the infused FEP was first modified. This is consistent with the results above which demonstrate the desirability of modifying the fluoropolymer surface to obtain a coating of silicon oxide above the surface of the fluoropolymer.

TABLE 2

Sample	%Fluorine	%Carbon	%Silicon	% Oxygen
Modified FEP (90 sec RFGD)	58.0	39.2	-	2.8
Modified FEP + SiCl ₄ Infusion	55.5	35.5	1.8	7.2
Unmodified FEP infused with SiCl ₄	64	33.4	0.3	2.2
FEP Infused with SiCl ₄ + 2 min RFGD	46.3	46.7	0.1	6.9

Example 22 -- Infusion Into Modified and Unmodified Fluoropolymers

The results listed in Table 3 illustrate that infusion of metals and metal oxides, (as demonstrated in this example using SiCl₄) into the bulk of halopolymers can be effected so that by first modifying the surface layer of the halopolymer one can achieve the bonding of the infused metal or metal oxide material not only within the bulk but at the surface of the halopolymer as well. This is further demonstrated by ESCA (or XPS) results which show more than two forms of oxygen and silicon at the surface of these materials. Because the sampling depth of the ESCA experiment allows one to observe molecular and polymeric species both at the surface as well as in the interfacial bulk of any inspected material, one can discern

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the differences in material lying within the bulk and at the air interface.

Accordingly, the experiments above show multiple spectroscopic bands for both the oxygen 1s and the silicon 2p functionality as observed in the materials which have been infused. Essentially, the modified materials exhibit only one oxygen band related to the incorporation of oxygen due to the surface modification achieved using the H₂/MeOH RFGD modification (except in the case of the MFA material, which initially includes an oxygen functionality due to the perfluoroalkoxy functionality included within its polymeric structure). Upon infusion of SiCl₄, and its subsequent hydrolysis to a silicate material, at least one other oxygen band by ESCA (in some cases more than one) was observed. These extra bands are believed to be due to the formation of silicon oxides of different structures within the polymer as well as the silicon oxide formed at the surface. For example, a silicon oxide within the bulk material may be directly influenced by the electronegative characteristics of the electron withdrawing halogen functionality, thus giving it a different binding energy relative to the one measured from the silicon oxide species covalently attached and proliferated at the surface of the active oxidized halogenated polymer. This is demonstrated in following examples as well which show the difference between infusion of non-surface modified halopolymers versus infusion of halopolymers which have been previously modified to include surface reactive oxygen functionalities.

TABLE 3

<u>Sample</u>	<u>%Carbon</u>	<u>%Oxygen</u>	<u>%Fluorine</u>	<u>%Silicon</u>	<u>%Chlorine</u>
PTFE modified	34.3	2.0	63.7	N/A	N/A
PTFE modified plus SiCl ₄ infusion	34.2	10.1	52.9	2.8	N/A
MFA modified	36.0	3.6	60.4	N/A	N/A
MFA modified plus SiCl ₄ infusion	28.2	28.1	34.5	9.2	N/A
ECTFE modified	69.8	9.0	19.3	N/A	1.8
ECTFE plus SiCl ₄ infusion	43.0	33.1	13.8	9.0	1.1

Example 23 -- Modified ECTFE and Unmodified ECTFE Infused With SiCl_4

ESCA results of infusing SiCl_4 into both modified and unmodified ECTFE indicate that the atomic percent of surface residing Si (which is related to the concentration of surface metal oxide) is greater in the case when the ECTFE material is modified versus the unmodified ECTFE material. Specifically, the % silicon (strictly due to the silicon oxide) increases from 2.5% to 9.0% in the case where the ECTFE material was first modified. Correspondingly, the oxygen % increases from 8.9% to 33.1% (again the increase is observed on the ECTFE material), indicating a large increase in surface residing silicon oxide which is due to the effect of initially modifying the ECTFE which results in an overcoating of covalently bonded silicon oxide to the modified ECTFE surface. This overcoating is not observed to the same extent on the unmodified ECTFE infused material.

Example 24 -- Unmodified and Surface Modified Halopolymers Infused With TiCl_4

A variety of surface modified and unmodified halopolymers were infused with TiCl_4 and then hydrolyzed to form nanoscale networks of titanium oxide material in the bulk of the halopolymers as well as at the surface of the modified halopolymers. The infusion process was carried out by placing films of the halopolymers into a glass vessel, evacuating the vessel to ca 10 mTorr or less, then introducing TiCl_4 into the evacuated vessel, and then heating the vessel to 90 °C. After 1 hr, the halopolymer films were removed to ambient air and then first ultrasonically washed in distilled H_2O for 30 min and then ultrasonically washed in MeOH for 30 min.

ESCA analysis was performed on these halopolymer films, and the results were obtained from three different halopolymer films, namely, PTFE, MFA, and ECTFE. For each material, data were collected from two separate films: one which was infused without prior surface modification and one which was infused after a H_2/MeOH RFGD surface modification.

Infusion of Modified and Unmodified PTFE. The modified PTFE was prepared using a 4 min exposure time to a H_2/MeOH RFGD plasma as described hereinabove as the preferred method of halopolymer surface modification. ESCA results showed that the % of titanium measured on the surface of these materials

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increased from 0.25% (measured on the non-surface modified PTFE) to 0.60 (measured on the surface modified PTFE). The % oxygen due to the titanium oxide increased from 4.1% (measured on the non-surface modified PTFE) to 7.8% (measured on the surface modified PTFE). These results indicate the desirability of first modifying the PTFE surface in order to extend the growth of titanium oxide (formed within the bulk of the PTFE) out of the bulk and onto the PTFE surface. ESCA results also reveal the presence of two oxygen bands (one at 536.4 eV due to the oxide contained in the bulk and one at 532.0 eV due to the surface residing oxide) and two titanium bands (one at 459.9 eV due to bulk titanate and one at 456.2 eV due to surface residing titanate). As discussed previously, the observation of two oxygen and two titanium bands is indicative of the formation of titanium oxide in the bulk which is heavily influenced by the PTFE electronegative functionality and the formation of titanium oxide out of the bulk such that it exists as a homogeneous material which has different electronic characteristics which give rise to oxygen and titanium ESCA signals significantly different than those of the titanium oxide material residing in the PTFE bulk.

Infusion of Modified and Unmodified MFA. The modified MFA was prepared using a 3 min exposure time to a H₂/MeOH RFGD plasma as described hereinabove as the preferred method of halopolymer surface modification. ESCA results showed that the % of titanium measured on the surface of these materials increased five-fold from 0.20% (measured on the non-surface modified MFA) to 1.00 (measured on the surface modified MFA). The % oxygen due to the titanium oxide increased from 8.9% (measured on the non-surface modified MFA) to 10.25% (measured on the surface modified MFA). These results indicate the desirability of first modifying the MFA surface in order to extend the growth of titanium oxide (formed within the bulk of the MFA) out of the bulk and onto the MFA surface. ESCA results also reveal the presence of three oxygen bands (one at 536.1 eV due to the titanium oxide contained in the bulk, a second at 533.4 eV due to the perfluoroalkoxy functionality contained within the MFA material, and a third at 531.4 eV due to the surface residing titanium oxide) and two titanium bands (one at 459.4 eV due to bulk titanate and one at 455.7 eV due to surface residing titanate). As discussed previously, the observation of two oxygen and two titanium bands is

indicative of the formation of titanium oxide in the bulk which is heavily influenced by the MFA electronegative functionality and the formation of titanium oxide out of the bulk such that it exists as a homogeneous material which has different electronic characteristics which give rise to oxygen and titanium ESCA signals significantly different than those of the titanium oxide material residing in the MFA bulk.

Infusion of Modified and Unmodified ECTFE. The modified ECTFE was prepared using a 90 sec exposure time to a H₂/MeOH RFGD plasma as described hereinabove as the preferred method of halopolymer surface modification. ESCA results showed that the % of titanium measured on the surface of these materials increased two-fold from 0.50% (measured on the non-surface modified ECTFE) to 1.00 (measured on the surface modified ECTFE). The % oxygen due to the titanium oxide increased from 4.3% (measured on the non-surface modified ECTFE) to 10.90% (measured on the surface modified ECTFE). These results indicate the desirability of first modifying the ECTFE surface in order to extend the growth of titanium oxide (formed within the bulk of the ECTFE) out of the bulk and onto the ECTFE surface. ESCA results also reveal the presence of two oxygen bands (one at 534.7 eV due to the titanium oxide contained in the bulk and another at 531.1 eV due to the surface residing titanium oxide) and two titanium bands (one at 457.2 eV due to the bulk titanate and another at 455.2 eV due to surface residing titanate). As discussed previously, the observation of two oxygen and two titanium bands is indicative of the formation of titanium oxide in the bulk which is heavily influenced by the ECTFE electronegative functionality and the formation of titanium oxide out of the bulk such that it exists as a homogeneous material which has different electronic characteristics which give rise to oxygen and titanium ESCA signals significantly different than those of the titanium oxide material residing in the ECTFE bulk.

Example 25 -- Infusion of Polymers for Decreasing the Permeability of Liquids and Gases

In many cases, it is useful to decrease the permeation of liquids and gases through polymeric materials. For example, U.S. Patent No. 5,298,291 to Klinger et al., which is hereby incorporated by reference, describes an epoxy-functional

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fluoropolyol polyacrylate coating of optical fibers as being useful as a moisture inhibitor and for inhibiting permeation of water through the polymeric network, thus preventing moisture-induced corrosion of the underlying fiberoptic material. As another example, U.S. Patent No. 5,320,888 to Stevens, which is hereby incorporated by reference, describes laminates of fluoroelastomers, non-elastomeric fluoropolymers, and non-fluorinated elastomers as being both flexible and useful for inhibiting the permeation of fuel. The composites of the present invention and composites made in accordance with the methods of the present invention are believed to be useful in inhibiting permeation of both gases and liquids. Both halopolymers (including elastomeric and non-elastomeric halopolymers) and non-halopolymers can be infused with metals and/or metal oxides, which can act to fill the free volumes of the halopolymers or non-halopolymers, thus increasing the polymer's density and blocking the permeation of both gases and liquids. The degree to which permeation of gases and liquids is inhibited can be controlled by the choice of metal and/or metal oxide and by the extent to which the metal and/or metal oxide is grown within the free volume within the halopolymer or non-halopolymer.

For example, 0.1g of TaF_5 was placed into a glass vessel containing a halopolymer film of ECTFE, which film had a density of 1.26 g/cm^3 . The vessel was evacuated to a pressure of less than 10 mTorr and then heated to ca. 150°C . After 1 hr, the film was removed from the vessel and ultrasonicated in distilled H_2O for 30 min and then ultrasonicated in MeOH for 30 min. After the sample was dried, it was weighed and the density was calculated to be 1.51 g/cm^3 . Thus the formation of tantalum oxide resulted in an increase in density of 16%.

Measurements of the amount of TaO_x showed that the amount of TaO_x added to the ECTFE film was approximately 2% by weight with the corresponding increase in density to be 16%. This material is expected to show significant decreases in gas and liquid permeability based on the measured increase in film density.

Alternatively, several grams of ECTFE powder (having diameters between 1 micron and 10 microns) were reacted with TaF_5 in the same way as described above for the ECTFE film. After infusion of TaF_5 , the TaF_5 was converted to TaO_x by hydrolysis. The powder is believed to be useful for coating objects either by

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thermally spraying or plasma spraying. The sprayed coating will have the same properties as that of the infused ECTFE film and will result in a coating having decreased gas and liquid permeability characteristics as compared to a sprayed coating of ECTFE which was not infused with TaO_x.

5 Additionally, the infused ECTFE powder can be surface modified either before or after infusion using any of the methods described herein (preferably the H₂/MeOH RFGD plasma treatment method) in order to provide surface wettability and/or good adhesion characteristics. These surface modified infused powders can then be used to coat other materials, for example by thermal or plasma spray
10 techniques or (since the surface is more wettable and adhesive) through mixing of the powders into paints, lacquers, or other resins which can be applied, for example, by rolling, brushing, or spraying.

 Although the invention has been described in detail for the purpose of illustration, it is understood that such detail is solely for that purpose, and variations
15 can be made therein by those skilled in the art without departing from the spirit and scope of the invention which is defined by the following claims.

WHAT IS CLAIMED:

1. A method for making a composite comprising:
providing a polymer having free volume therein;
evacuating the free volume of the polymer; and
infusing inorganic or organic molecules into the evacuated free volume of the polymer.
2. A method according to claim 1, wherein the free volume of the polymer is the polymer's natural free volume.
3. A method according to claim 1 further comprising:
polymerizing the inorganic or organic molecules under conditions effective to assemble the inorganic or organic molecules into macromolecular networks.
4. A method according to claim 3, wherein said polymerizing is carried out photochemically, chemically, or electrochemically.
5. A method according to claim 3, wherein said polymerizing is carried out by oxidizing, hydrolyzing, or hydrogenating the inorganic or organic molecules.
6. A method according to claim 5 wherein the oxidizing, hydrolyzing, or hydrogenating comprises:
exposing the inorganic or organic molecules to a gas comprising water, oxygen, hydrogen, or combinations thereof.
7. A method according to claim 6, wherein said polymerizing is carried out by oxidizing or hydrolyzing the inorganic or organic molecules and wherein the gas is ambient air.

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8. A method according to claim 3, wherein the inorganic or organic molecules are inorganic molecules comprising metal atoms and ligands bonded thereto which can be cleaved from the metal atoms by exposure to actinic radiation and wherein said polymerizing comprises:

exposing the inorganic molecules to actinic radiation under conditions effective to cleave the ligands from the metal atoms and

exposing the metal atoms having ligands cleaved therefrom to an oxygen-containing or water-containing gas under conditions effective to cause the metal atoms to assemble into macromolecular networks.

9. A method according to claim 3, wherein the inorganic or organic molecules are pi-allyl compounds of Group IIIa, IVa, Va, VIa, VIIa, or VIIIa metals and wherein said polymerizing comprises:

contacting the pi-allyl compounds with hydrogen gas under conditions effective to cause the formation of a conductive zero-valent macromolecular metal network.

10. A method according to claim 1, wherein the polymer comprises a functionality and wherein said method further comprises treating the inorganic or organic molecules under conditions effective to cause the inorganic or organic molecules to interact with the polymer's functionality.

11. A method according to claim 10, wherein the functionality is a halogen atom.

12. A method according to claim 10, wherein the functionality is a fluorine atom.

13. A method according to claim 10, wherein said treating is carried out photochemically, chemically, or electrochemically.

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14. A method according to claim 10, wherein said treating comprises oxidizing, hydrolyzing, or hydrogenating the inorganic or organic molecules

15. A method according to claim 14, wherein the oxidizing, hydrolyzing, or hydrogenating comprises:

exposing the inorganic or organic molecules to a gas comprising water, oxygen, hydrogen, or combinations thereof.

16. A method according to claim 15, wherein said treating is carried out by oxidizing or hydrolyzing the inorganic or organic molecules and wherein the gas is ambient air.

17. A method according to claim 10, wherein the inorganic or organic molecules are inorganic molecules comprising metal atoms and ligands bonded thereto which can be cleaved from the metal atoms by exposure to actinic radiation and wherein said treating comprises:

exposing the inorganic molecules to actinic radiation under conditions effective to cleave the ligands from the metal atoms and

treating the metal atoms having ligands cleaved therefrom photochemically, chemically, electrochemically, or thermally under conditions effective to cause the metal atoms to interact with the polymer's functionality.

18. A method according to claim 1, wherein said infusing is carried out under non-supercritical conditions.

19. A method according to claim 1, wherein the inorganic or organic molecules are infused into the free volume of the polymer in a gaseous state.

20. A method according to claim 1, wherein said infusing comprises:
vaporizing the inorganic or organic molecules to produce an inorganic or organic molecule vapor; and

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contacting the polymer with the inorganic or organic molecule vapor.

21. A method according to claim 1, wherein the polymer comprises halopolymers, polyimides, polyamides, polyalkylenes, poly(phenylenediamine terephthalamide) filaments, polyethyleneterephthalates, modified cellulose derivatives, starch, polyesters, polymethacrylates, polyacrylates, polyvinyl alcohol, copolymers of vinyl alcohol with ethylenically unsaturated monomers, polyvinyl acetate, poly(alkylene oxides), vinyl chloride homopolymers and copolymers, terpolymers of ethylene with carbon monoxide and with an acrylic acid ester or vinyl monomer, polysiloxanes, homopolymers and copolymers of halodioxoles and substituted dioxoles, polyvinylpyrrolidone, or combinations thereof.

22. A method according to claim 1, wherein the polymer comprises a halopolymer.

23. A method according to claim 22, wherein the polymer comprises a fluoropolymer.

24. A method according to claim 1, wherein the polymer has a crystallinity of less than about 99%.

25. A method according to claim 1, wherein the polymer has a glass transition temperature of T_g and a thermal decomposition temperature of T_d and wherein said infusing is carried out at a temperature from about $T_g - 50^\circ\text{C}$ to about T_d and at which the inorganic or organic molecules have a non-zero vapor pressure.

26. A method according to claim 1, wherein the inorganic or organic molecules are selected from the group consisting of VOCl_3 , $\text{W}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$, TiCl_4 , SiCl_4 , AlCl_3 , PCl_3 , SbCl_5 , $\text{As}(\text{C}_2\text{H}_5)_3$, $\text{Ba}(\text{C}_3\text{H}_7)_2$, borane pyridine and tetrahydrofuran complexes, $\text{Cd}(\text{BF}_4)_2$, $\text{Ca}(\text{OOCCH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9)_2$, cerium (III) 2-ethylhexanoate, cesium 2-ethylhexoxide, chromium (III) naphthenate, CrO_2Cl_2 , $\text{Co}(\text{CO})_3\text{NO}$, copper

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(II) dimethylaminoethoxide, triethylgallium, GeCl_4 , triethylindium, lead naphenate, $\text{C}_2\text{H}_5\text{MgCl}$, $(\text{CH}_3)_2\text{Hg}$, MoF_6 , $\text{Ni}(\text{CO})_4$, $\text{Nb}(\text{OC}_2\text{H}_5)_6$, HReO_4 , $\text{Ta}(\text{OC}_2\text{H}_5)_5$, $\text{C}_5\text{H}_5\text{Tl}$, SnCl_4 , pi-allyl compounds of Group IIIa, IVa, Va, VIa, VIIa, or VIIIa metals, and combinations thereof.

27. A method according to claim 1, wherein the composite has flexibility, crystallinity, or thermal decomposition temperature which is substantially the same as those of the polymer.

28. A method according to claim 27, further comprising:
treating the composite thermally, chemically, photochemically, or electrochemically under conditions effective to alter a physical, chemical, optical, or electrical property of the composite.

29. A composite comprising:
a polymer having natural free volume therein;
and an inorganic or organic material disposed in the natural free volume of said polymer.

30. A composite according to claim 29, wherein said composite has dimensions which are substantially equal to the dimensions of said polymer.

31. A composite according to claim 29, wherein said natural free volume contains substantially no carrier liquid.

32. A composite according to claim 29 having flexibility, crystallinity, or thermal decomposition temperature which is substantially the same as those of said polymer.

33. A composite according to claim 29, wherein the natural free volume is defined by free volume surfaces and wherein said inorganic or organic material is present as a layer on or along the free volume surfaces.

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34. A composite according to claim 29, wherein said polymer comprises a functionality and wherein said inorganic or organic material interacts with the polymer's functionality.

35. A composite according to claim 34, wherein the functionality is a halogen atom.

36. A composite according to claim 34, wherein the functionality is a fluorine atom.

37. A composite according to claim 29, wherein said inorganic or organic material is an inorganic or organic macromolecular network.

38. A composite according to claim 37, wherein the inorganic or organic macromolecular network is an inorganic macromolecular network.

39. A composite according to claim 38, wherein the inorganic macromolecular network has the formula $[X(O)_n-O_y-X(O)_n]_m$, wherein m is an integer from about 1 to about 10,000; X represents a metal ion having a charge of +s; s is an integer from 1 to the metal's highest attainable oxidation state; y is an integer from 0 to s; and n is between zero and s/2.

40. A composite according to claim 38, wherein the inorganic macromolecular network is a conductive zero-valent macromolecular metal network containing a Group IIIa, IVa, Va, VIa, VIIa, or VIIIa metal.

41. A composite according to claim 37, wherein the inorganic or organic macromolecular network is an organic macromolecular network.

42. A composite according to claim 40, wherein the organic macromolecular network has the formula $(R-R)_n$, wherein n is an integer from about 1 to about 10,000 and R is a monomer radical.

43. A composite according to claim 40, wherein the organic macromolecular network comprises polyacetylene, polypyrrole, polyaniline, polythiophene, or combinations thereof.

44. A composite according to claim 29, wherein said polymer comprises halopolymers, polyimides, polyamides, polyalkylenes, poly(phenylenediamine terephthalamide) filaments, polyethyleneterphthalates, modified cellulose derivatives, starch, polyesters, polymethacrylates, polyacrylates, polyvinyl alcohol, copolymers of vinyl alcohol with ethylenically unsaturated monomers, polyvinyl acetate, poly(alkylene oxides), vinyl chloride homopolymers and copolymers, terpolymers of ethylene with carbon monoxide and with an acrylic acid ester or vinyl monomer, polysiloxanes, homopolymers and copolymers of halodioxoles and substituted dioxoles, polyvinylpyrrolidone, or combinations thereof.

45. A composite according to claim 29, wherein said polymer comprises a halopolymer.

46. A composite according to claim 45, wherein said polymer comprises a fluoropolymer.

47. A composite according to claim 29, wherein said polymer has a crystallinity of less than about 99%.

48. A composite according to claim 29 having a volume of V_c , wherein the natural free volume is greater than about $1 \times 10^{-6} V_c$.

49. A composite according to claim 29, wherein said inorganic or organic material is an inorganic material comprising a metal selected from the group consisting of V, W, Fe, Ti, Si, Al, P, Sb, As, Ba, B, Cd, Ca, Ce, Cs, Cr, Co, Cu, Ga, Ge, In, Pb, Mg, Hg, Mo, Ni, Nb, Re, Ta, Tl, Sn, Ir, Rh, Th, Ru, Os, Pd, Pt, Zn, Au, Ag, and combinations thereof.

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50. A method of catalyzing a reaction of a reactant comprising:
providing a composite according to claim 29, wherein the inorganic or organic material is suitable for catalyzing the reaction of the reactant;
and
contacting the composite with the reactant under conditions effective to catalyze the reaction.
51. A method according to claim 50, wherein the reactant is a gaseous reactant.
52. A method according to claim 51, wherein the reactant is SO₂ and the inorganic or organic material is an inorganic macromolecular network comprising vanadium.
53. A method according to claim 51, wherein said contacting is carried out under supercritical conditions.
54. A method according to claim 51, wherein the reaction is an oxidation reaction, the reactant is an oxidizable substrate and wherein said contacting is carried out in the presence of an oxidizing agent.
55. A method according to claim 54, wherein the oxidizable substrate is methanol and wherein said method produces formaldehyde and formic acid.
56. A method according to claim 54, wherein the oxidizable substrate is o-xylene and wherein said method produces phthalic anhydride.
57. A method according to claim 54, wherein the oxidizing agent is oxygen.
58. A method according to claim 54, wherein said method is carried out in the presence of a co-reductant.

59. A method according to claim 54, wherein the polymer is a fluoropolymer.

60. A method according to claim 54, wherein the inorganic material comprises vanadium or titanium.

61. A electroconductive imaging element comprising:
an insulating support;
an electrically-conductive layer overlaying the support, wherein said electrically-conductive layer comprises a composite of claim 29; and
a dielectric imaging layer overlaying the electrically-conductive layer.

62. A photographic element comprising:
a substrate;
a light-sensitive layer directly or indirectly disposed on the substrate; and
an antistatic layer directly or indirectly disposed on the substrate, wherein the antistatic layer comprises a composite of claim 29.

63. A electrolytic fuel cell comprising:
a composite of claim 29;
an anode in electrical contact with the said composite; and
an cathode in electrical contact with the said composite.

64. A method for shielding a material from electromagnetic radiation emitted from an electromagnetic radiation source comprising:
disposing between the material and the electromagnetic radiation source a composite according to claim 29, wherein the inorganic or organic material comprises a metal.

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65. A method for shielding a material from heat or flame source comprising:

disposing between the material and the heat or flame source a composite according to claim 29, wherein the inorganic or organic material is a metal oxide.

66. A method for preventing fouling of a surface by organisms, said method comprising:

applying, to the surface, a composite comprising a polymer having free volume therein and an inorganic or organic material disposed in the free volume of the polymer.

67. A method according to claim 66, wherein the surface is the surface of a water-going vessel, a propeller, a pier, or a pipe.

68. A method according to claim 66, wherein the organisms are aerobic.

69. A method according to claim 66, wherein the organisms are marine organisms, aquatic organisms, or microbes.

70. A method according to claim 66, wherein the organisms are crustaceans or mussels.

71. A method according to claim 66, wherein the inorganic material is capable of catalytically splitting dioxygen.

72. A method according to claim 66, wherein the inorganic material comprises vanadium or titanium.

73. A method according to claim 66, wherein the surface is in continuous or intermittent contact with water.

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74. A method according to claim 66, wherein said applying comprises:
providing the composite in sheet form and contacting the composite in sheet form with the surface under conditions effective to attach the composite in sheet form to the surface.

75. A method according to claim 66, wherein said applying comprises:
providing the composite in bead or powder form dispersed in an uncured resin;
contacting the composite in bead or powder form dispersed in uncured resin with the surface; and
curing the uncured resin to a degree effective to attach the composite in bead or powder form to the surface.

76. A method according to claim 75, wherein said contacting comprises spraying, sputtering, painting, or dipping.

77. A method according to claim 66, wherein said applying comprises:
applying uncured resin to the surface;
contacting the composite in bead or powder form with the uncured resin; and
curing the uncured resin to a degree effective to attach the composite in bead or powder form to the surface.

78. A method according to claim 66, wherein said applying comprises:
providing the composite in bead or powder form dispersed in a suitable solvent;
contacting the composite in bead or powder form dispersed in suitable solvent with the surface; and
evaporating the solvent.

79. A method according to claim 66, wherein said applying comprises:
coating the composite in bead or powder form directly on the surface

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via thermally based spraying, sputtering, or dipping or via use of high-temperature plasma spray technology.

80. A method according to claim 66, wherein the polymer comprises a fluoropolymer.

81. A method for preventing fouling of a polymer surface by organisms, wherein the polymer surface comprises a polymer having free volume therein, said method comprising:

evacuating the free volume of the polymer; and
infusing inorganic or organic molecules into the evacuated free volume of the polymer.

82. A method according to claim 81, wherein the polymer surface is the polymer surface of a water-going vessel, a propeller, a pier, or a pipe.

83. A method according to claim 81, wherein the organisms are aerobic.

84. A method according to claim 81, wherein the organisms are marine organisms, aquatic organisms, or microbes.

85. A method according to claim 81, wherein the organisms are crustaceans or mussels.

86. A method according to claim 81, wherein the inorganic material is capable of catalytically splitting dioxygen.

87. A method according to claim 81, wherein the inorganic material comprises vanadium or titanium.

88. A method according to claim 81, wherein the surface is in continuous or intermittent contact with water.

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89. A method according to claim 81, wherein the polymer comprises a fluoropolymer.

90. An object having a surface, wherein all or a portion of said surface comprises a polymer having free volume therein and an inorganic or organic material disposed in the free volume of the polymer.

91. An object according to claim 90, wherein the surface is in continuous or intermittent contact with water.

92. An object according to claim 90, said object being a water-going vessel comprising:

a hull, said hull having an exterior surface; and

a composite comprising a polymer having free volume therein and an inorganic or organic material disposed in the free volume of the polymer, wherein said composite is attached to at least a portion of said hull's exterior surface.

93. An object according to claim 90, said object being a pipe comprising:

a pipe wall having an interior surface and an exterior surface; and

a composite comprising a polymer having free volume therein and an inorganic or organic material disposed in the free volume of the polymer, wherein said composite is attached to at least a portion of said pipe wall's interior surface, exterior surface, or both.

94. An object according to claim 90, said object being a stationary structure comprising:

a support having a surface, said surface being in continuous or intermittent contact with water; and

a composite comprising a polymer having free volume therein and an inorganic or organic material disposed in the free volume of the polymer, wherein said composite is attached to at least a portion of said support's surface.

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95. An object according to claim 94, wherein the stationary structure is selected from the group consisting of drilling platforms, oil production rigs, bridges, and piers.

96. An object according to claim 90, wherein the inorganic or organic material is an inorganic or organic macromolecular network.

97. An object according to claim 90, wherein the inorganic material comprises vanadium or titanium.

98. A method for making an oxyhalopolymer composite comprising:
providing an oxyhalopolymer having free volume therein;
evacuating the free volume of the oxyhalopolymer; and
infusing inorganic or organic molecules into the evacuated free volume of the oxyhalopolymer.

99. A method according to claim 98, wherein said providing the oxyhalopolymer comprises:
providing a halopolymer;
modifying the halopolymer's surface halogen atoms under conditions effective to substitute at least a portion of the halopolymer's surface halogen atoms with hydrogen atoms and oxygen atoms or oxygen-containing radicals.

100. A method according to claim 99, wherein the halopolymer's surface halogen atoms are modified by radio frequency glow discharge of a gas-vapor under vacuum comprising:

contacting the halopolymer with a gas/vapor plasma mixture while exposing the halopolymer to at least one radio frequency glow discharge under vacuum under conditions effective to substitute at least a portion of the halopolymer's halogen atoms with covalently bonded hydrogen atoms and oxygen atoms or oxygen-containing radicals.

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101. A method for making an oxyhalopolymer composite comprising:
providing a halopolymer composite; and
modifying the halopolymer composite's surface halogen atoms under conditions effective to substitute at least a portion of the halopolymer composite's surface halogen atoms with hydrogen atoms and oxygen atoms or oxygen-containing radicals.

102. A method according to claim 101, wherein said providing the halopolymer composite comprises:
providing an halopolymer having free volume therein;
evacuating the free volume of the halopolymer; and
infusing inorganic or organic molecules into the evacuated free volume of the halopolymer.

103. A method according to claim 101, wherein the halopolymer composite's surface halogen atoms are modified by a radio frequency glow discharge of a gas-vapor under vacuum comprising:
contacting the halopolymer composite with a gas/vapor plasma mixture while exposing the halopolymer composite to at least one radio frequency glow discharge under vacuum and under conditions effective to substitute at least a portion of the halopolymer composite's surface halogen atoms with covalently bonded hydrogen atoms and oxygen atoms or oxygen-containing radicals.

104. A method for making a surface-oxyhalogenated non-halopolymer composite comprising:
providing a surface-oxyhalogenated non-halopolymer having free volume therein;
evacuating the free volume of the surface-oxyhalogenated non-halopolymer; and
infusing inorganic or organic molecules into the evacuated free volume of the surface-oxyhalogenated non-halopolymer.

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105. A method according to claim 104, wherein said providing the surface-oxyhalogenated non-halopolymer comprises:

providing a surface-halogenated non-halopolymer having free volume therein; and

modifying the surface-halogenated non-halopolymer's surface halogen atoms under conditions effective to substitute at least a portion of the surface-halogenated non-halopolymer's surface halogen atoms with hydrogen atoms and oxygen atoms or oxygen-containing radicals.

106. A method according to claim 105, wherein said providing a surface-halogenated non-halopolymer comprises:

providing a non-halopolymer having free volume therein; and

contacting the non-halopolymer's surface with halogen atoms or a halocarbon or halohydrocarbon film under conditions effective to molecularly bond the halogen atoms or the halocarbon or halohydrocarbon film to the non-halopolymer's surface.

107. A method according to claim 105, wherein the surface-halogenated non-halopolymer's surface halogen atoms are modified by radio frequency glow discharge of a gas-vapor under vacuum comprising:

contacting the surface-halogenated non-halopolymer with a gas/vapor plasma mixture while exposing the surface-halogenated non-halopolymer to at least one radio frequency glow discharge under vacuum under conditions effective to substitute at least a portion of the surface-halogenated non-halopolymer's surface halogen atoms with covalently bonded hydrogen atoms and oxygen atoms or oxygen-containing radicals.

108. A method according to claim 104, wherein the surface-oxyhalogenated non-halopolymer comprises a non-halopolymer having a surface that is modified with a halocarbon or halohydrocarbon film, wherein both of the non-halopolymer and the halocarbon or halohydrocarbon film have free volumes therein and wherein said method further comprises:

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evacuating the free volume of the halocarbon or haloalkane film;
and
infusing inorganic or organic molecules into the evacuated free
volume of the halocarbon or haloalkane film.

109. A method for making a surface-oxyhalogenated non-halopolymer
composite comprising:

providing a surface-halogenated non-halopolymer composite; and
modifying the surface-halogenated non-halopolymer composite's
surface halogen atoms under conditions effective to substitute at least a portion of
the surface-halogenated non-halopolymer composite's surface halogen atoms with
hydrogen atoms and oxygen atoms or oxygen-containing radicals.

110. A method according to claim 109, wherein said providing a surface-
halogenated non-halopolymer composite comprises:

providing a surface-halogenated non-halopolymer having free volume
therein;

evacuating the free volume of the surface-halogenated non-
halopolymer; and

infusing inorganic or organic molecules into the evacuated free
volume of the surface-halogenated non-halopolymer.

111. A method according to claim 109, wherein the surface-halogenated
non-halopolymer comprises a non-halopolymer having a surface that is modified
with a halocarbon or haloalkane film, wherein both the non-halopolymer and
the halocarbon or haloalkane film have free volumes therein and wherein said
method further comprises:

evacuating the free volume of the halocarbon or haloalkane film;
and

infusing inorganic or organic molecules into the evacuated free
volume of the halocarbon or haloalkane film.

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112. A method according to claim 109, wherein said providing a surface-halogenated non-halopolymer composite comprises:

providing a non-halopolymer composite; and

contacting the non-halopolymer composite's surface with halogen atoms or a halocarbon or halohydrocarbon film under conditions effective to molecularly bond the halogen atoms or the halocarbon or halohydrocarbon film to the non-halopolymer composite's surface.

113. A method according to claim 112, wherein said providing a non-halopolymer composite comprises:

providing a non-halopolymer having free volume therein;

evacuating the free volume of the non-halopolymer; and

infusing inorganic or organic molecules into the evacuated free volume of the non-halopolymer.

114. A method according to claim 109, wherein the surface-halogenated non-halopolymer composite's surface halogen atoms are modified by radio frequency glow discharge of a gas-vapor under vacuum comprising:

contacting the surface-halogenated non-halopolymer composite with a gas/vapor plasma mixture while exposing the surface-halogenated non-halopolymer composite to at least one radio frequency glow discharge under vacuum under conditions effective to substitute at least a portion of the surface-halogenated non-halopolymer composite's surface halogen atoms with covalently bonded hydrogen atoms and oxygen atoms or oxygen-containing radicals.

115. An oxyhalopolymer composite comprising:

an oxyhalopolymer having free volume therein; and

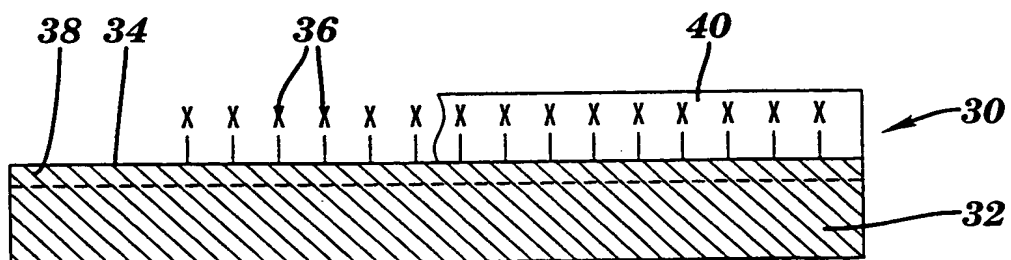
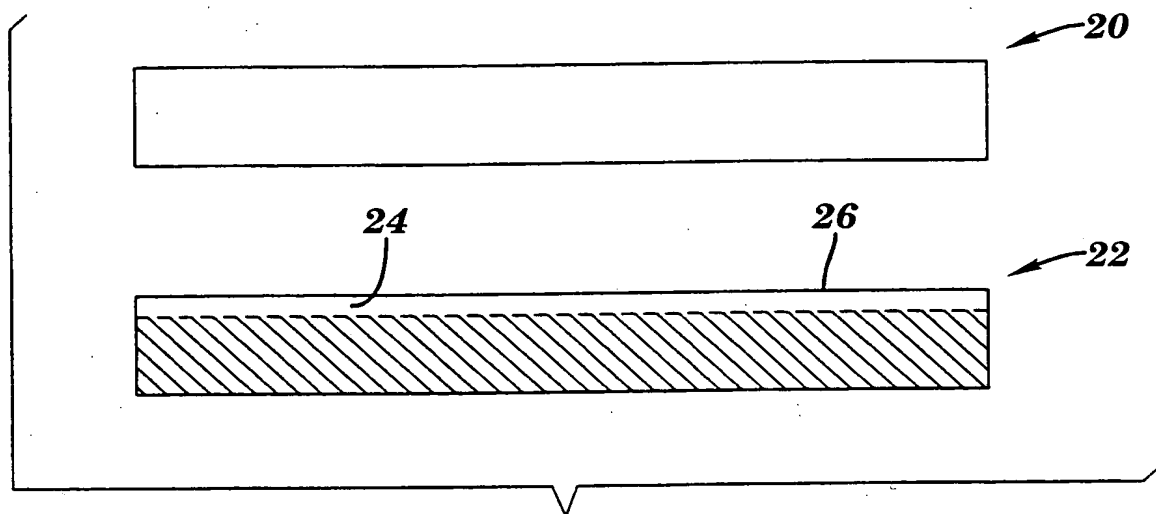
an inorganic or organic material disposed in the free volume of said oxyhalopolymer.

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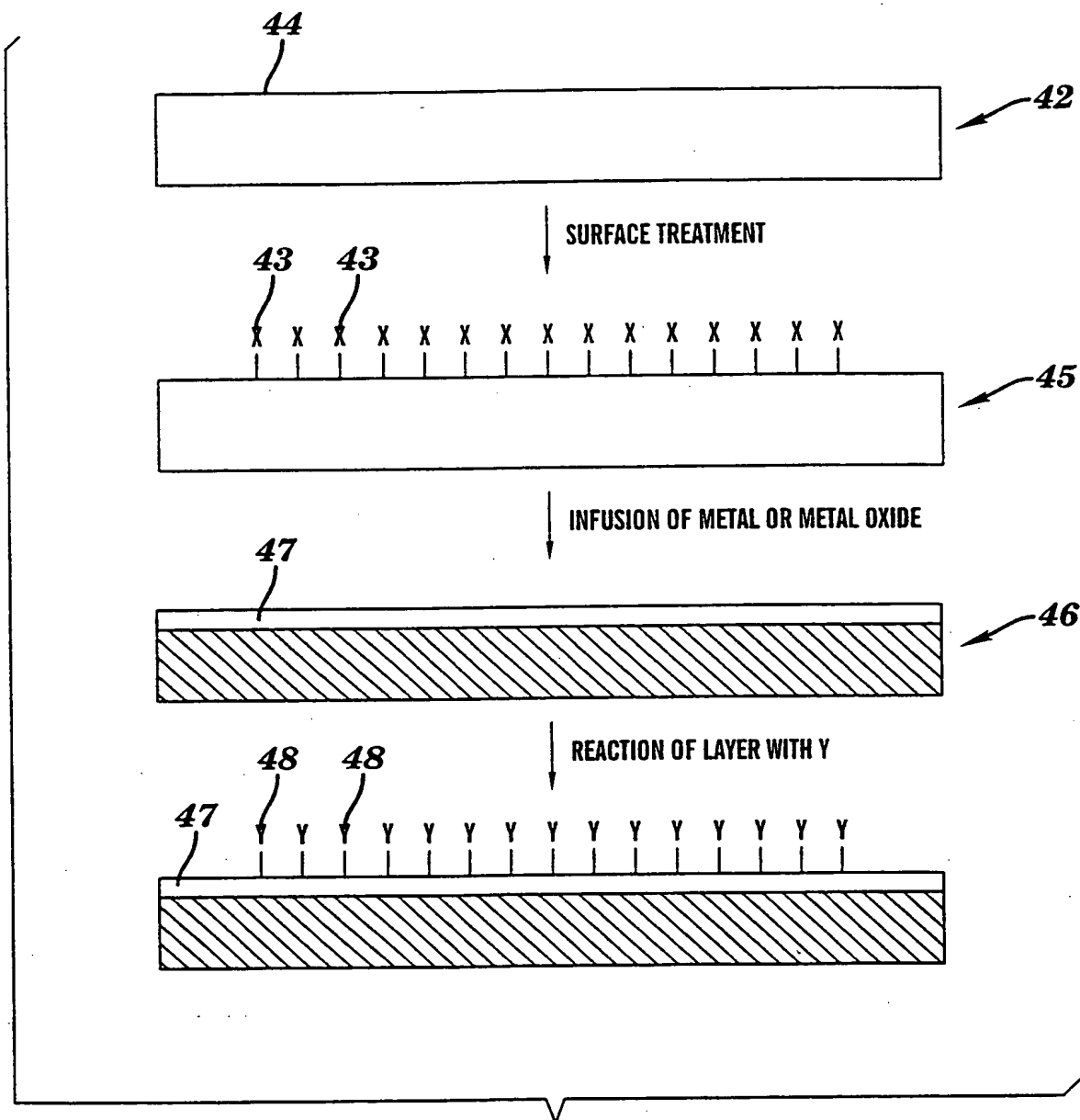
116. A surface-oxyhalogenated non-halopolymer composite comprising:
a surface-oxyhalogenated non-halopolymer having free volume
therein; and
an inorganic or organic material disposed in the free volume of said
surface-oxyhalogenated non-halopolymer.

117. A surface-oxyhalogenated non-halopolymer composite according to
claim 116, wherein said surface-oxyhalogenated non-halopolymer comprises a non-
halopolymer having a surface that is modified with a halocarbon or halohydrocarbon
film, wherein both the non-halopolymer and the halocarbon or halohydrocarbon film
have free volumes therein, and wherein the inorganic or organic material is disposed
in the free volume of the non-halopolymer and in the free volume of the halocarbon
or halohydrocarbon film.

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**FIG. 3**

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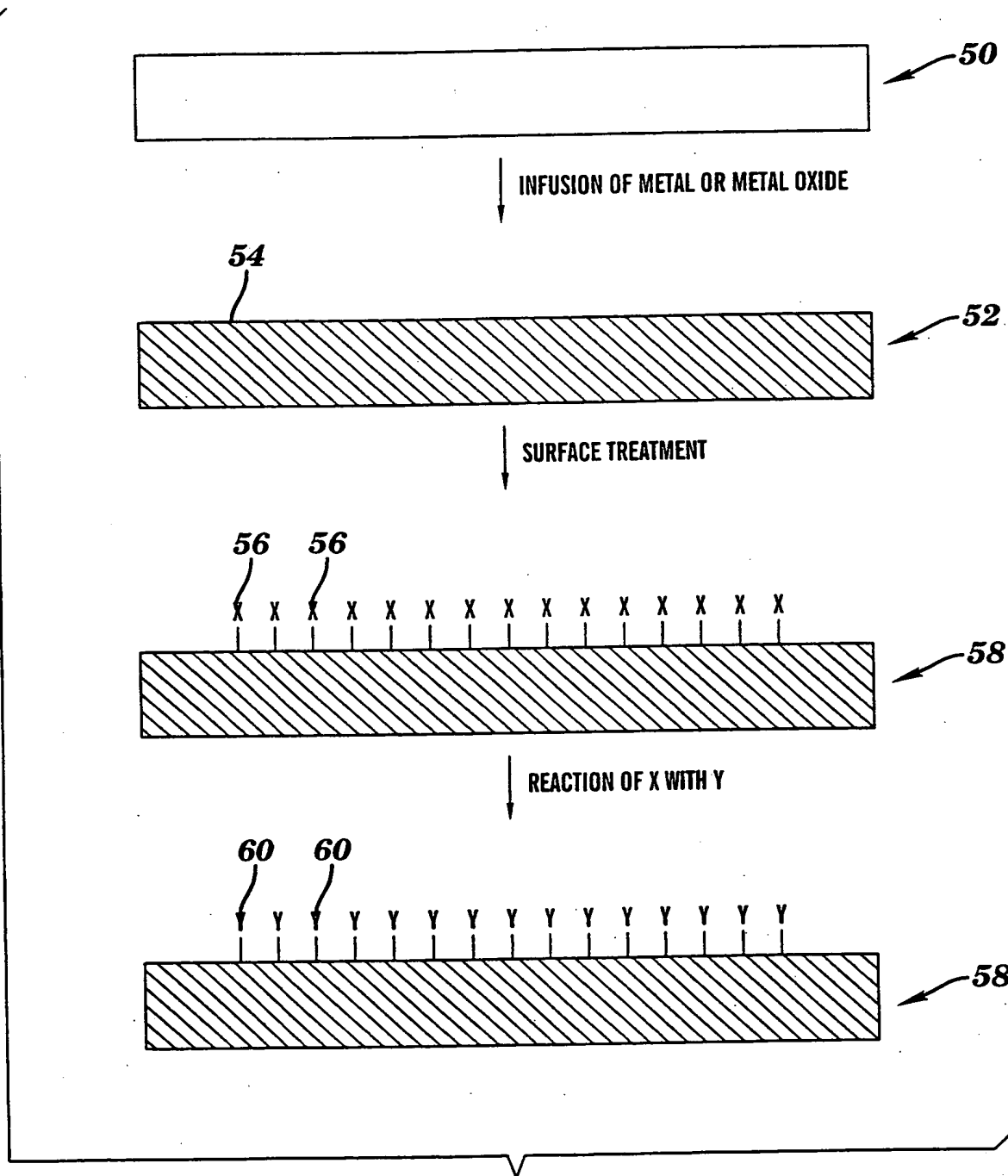


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03424

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/403, 430, 431, 433, 544, 546; 428/319.1, 319.3; 528/490, 502R; 502/349, 353

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 5,112,529 A (SAITO) 12 May 1992, abstract, column 3, line 49 to column 4, line 22 and column 5, lines 4-10.	1-2, 10-12, 18-21, 24-25, 27, 29-34, 47-48, 90-92, 95-96 ----- 1-2, 10-12, 18-21, 24-25, 27-34, 47-48, 90-92, 95-96

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

06 MAY 1998

Date of mailing of the international search report

01 JUN 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

ANDREW E.C. MERRIAM

Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/03424

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	PATCHORNIK et al, Caging of and Catalysis by a Complex inside a Polymer Matrix, J. Chem. Soc., Chem. Commun., 1990, pages 1090-1091.	1-2, 18, 24-25, 27, 29-33, 47-48, 50, 90-92, 96-98 ----- 1-2, 18, 24-25, 27, 29-33, 47-48, 50-51, 90-92, 96-98
X -- Y	US 5,420,313 A (CUNNINGTON et al) 30 May 1995, abstract, column 1, lines 5-14, column 2, lines 5-22, column 3, lines 19-60, column 4, lines 14-38, column 8, lines 53-69 and column 12, lines 1-40.	1-2, 18, 21, 24-25, 27, 29-33, 44, 47-48, 50, 90-92, 96-98 ----- 1-2, 18, 21, 24-25, 27, 29-33, 44, 47-48, 50-51, 54, 56-57, 90-92, 96-98
X -- Y	US 4,381,918 A (EHRNFORD) 03 May 1983, abstract, column 2, lines 10-20, column 3, lines 5-38, column 4, lines 5-17, column 7, lines 42-62 and column 8, lines 10-34.	1-5, 10, 14, 18, 21, 24-25, 27-34, 37, 47-48, 90-92 ----- 1-5, 10, 13-16, 18, 21, 24-25, 27-34, 37, 47-48, 90-92
X -- Y	US 4,865,925 A (LUDWIG et al) 12 September 1989, abstract, column 2, line 69 to column 3, line 10, column 3, line 44 to column 4, line 30, column 9, line 55 to column 10, line 36.	1-2, 10-14, 18-25, 27-37, 44-48, 90-92, 96, 99, 115-117 ----- 1-2, 10-14, 18-25, 27-37, 44-48, 90-92, 96-99, 104, 115-117

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03424

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-8, 10-16, 18-39, 44-48, 50-60

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03424

A. CLASSIFICATION OF SUBJECT MATTER: IPC (6):

B01J 23/00, 23/16; B32B 5/28, 27/20; C08K 3/10, 3/18, 3/22; C08L 23/26

A. CLASSIFICATION OF SUBJECT MATTER: US CL :

524/403, 430, 431, 433, 544, 546; 428/319.1, 319.3; 528/490, 502R; 502/349, 353

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-60, drawn to an infused polymeric composite and method for making and a process of use as a catalyst.

Group II, claim(s) 66-97, drawn to an antifouling polymeric article and method for making and using.

Group III, claim(s) 98-117, drawn to a method for treating a polymer to make an oxyhalopolymer composite and a product oxyhalopolymer composite.

Group IV, claims 61 and 64, drawn to an electroconductive composite element and a product composite for electromagnetic shielding.

Group V, claim 62, drawn to a photographic element product.

Group VI, claim 63, drawn to a fuel cell product, and

Group VII, claim 65, drawn to a heat shielding product.

The inventions listed as Groups I-VII do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

The special technical features of the antifouling article and method of Group II contributes over the prior art both a different utility and a different antifouling material than that of any of the other Groups;

the special technical features of the oxyhalopolymer composite Group III contributes over the prior art both a different polymer and a different method of reaction to make a polymer or composite than that of any of the other Groups;

the special technical features of each of the Groups IV-VII electroconductive and shielding element (Group IV), photographic element (Group V), fuel cell (Group VI) and heat shielding product (Group VII) contributes over the prior art a different method of use or function than that of any of the other Groups; and,

the special technical features of the Group I composite and catalyst product contributes over the prior art a catalyst method of use and a catalytic material that differs from the uses and materials of the any of the remaining Groups II-Vii.

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack Unity of Invention because they are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for more than one species to be searched, the appropriate additional search fees must be paid. The species are as follows:

Metal oxide materials (claims 26 and 37-39); organometallic materials (claims 9, 17 and 26); organic macromolecular materials (claims 37 and 41-43); and elemental metal materials (claims 40 and 49).

The species listed above do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features for the following reasons: Each of the four species listed has a distinct chemical structure, belongs to a distinct chemical class of compounds and serves a distinct purpose or utility. The organic macromolecules are conductive; the elemental metals are dielectric or shielding materials; the metal oxides are either catalytic or mechanically reinforcing; and the organometal compounds can be antibacterial or catalytic.